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# OVERAGE INDICATOR FOR GRAPHITE FIBER EPOXY PREPREG

Z. N. Sanjana
Principal Investigator

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Final Report for the Period
5 Jan. 79 to 5 Sept. 79
Contract No. N00019-78-C-0600

September 1979



Department of the Navy
Naval Air Systems Command
Washington, D.C. 20361



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Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

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Block No. 20 (Abstract)


Prepreg or B-staged products are used extensively in the aerospace, electrical, and communications industries. They consist of a partially reacted mixture of monomers which have been impregnated into the reinforcement. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or "age" of the prepreg will depend on the conditions (temperature, humidity and time) that it has been exposed to.

This report provides data and results of aging studies performed on Hercules 3501-6/AS graphite epoxy prepreg under diverse conditions of temperature, time and humidity. At various times during the aging, physical properties of the prepreg were measured and the following methods were used to track the age of the prepreg: (1) dielectric analysis (DA), (2) dynamic mechanical analysis (DMA), and (3) a simple, easy to use time-temperature integrating device (TTW) which is carried with the prepreg and provides a visual observation of the time and temperature exposure of the prepreg. Liquid chromatography (LC) was used to characterize some of the changes. It was found that DA, DMA, and the TTW can be used to follow the age of the prepreg and that they can be used as overage indicators to tell the user when the prepreg has lost its useful life.

The changes in prepreg reactivity caused by aging in a humid environment were also determined using DA and LC. This study was conducted by exposing prepreg to dry and humid conditions at different temperatures. Results indicate that exposure to high humidity will ultimately result in prepreg with much greater reactivity when compared to initial or dry aged prepreg. This change is irreversible and is time and temperature dependent.

## FOREWORD

The following final report describes work performed on NASC Contract No. N00019-78-C-0600, "Overage Indicator for Graphite Fiber Epoxy". The work accomplished and reported herein was performed by Westinghouse Electric Corp., R&D Center. The program was administered by M. Stander for the Naval Air Systems Command.

The program was conducted in the Polymers and Plastics Department, J. H. Freeman, Manager, with Z. N. Sanjana as principal investigator. Contributions to the program were also made by W. H. Schaefer and J. R. Ray.

This report covers the contract period 5 January 1979 to 5 September 1979.

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# 1. INTRODUCTION

The use of non-metallic materials for structural applications in high performance military aircraft is expanding. The principal non-metallics used are advanced composites and adhesives. The advanced composite material (usually graphite-epoxy) for structural application is generally obtained from the supplier as a prepreg or a B-staged product.

A prepreg product consists of a partially reacted mixture of monomers which has been impregnated into the reinforcement. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or "age" of the prepreg will depend on the conditions (principally, temperature, humidity and time) that it has been exposed to. These conditions are often unknown. At a point in the age of the prepreg, some critical property or properties will deteriorate. This would then represent the end of the useful life of the prepreg.

An overage indicator should reliably inform the user of a prepreg when its useful life is over. This requires that the useful life of the prepreg be defined. With an epoxy system, this often depends on the end use for the prepreg. If the user is only interested in making flat laminates, for example, the prepreg can be used well after the point at which it becomes stiff and boardy. If, however, the use requires laying up the prepreg in a complex shape, it must be soft and tacky so that it can be draped and it can adhere to itself. In general, the end point of the useful life of a prepreg occurs when some critical property begins to be adversely affected. The critical property concerned will depend upon the end use intended for the product.

The overage indicator then may be either the critical property itself or some other measurement which correlates well with the loss of the critical property. The latter affords more flexibility and generality of application since, as observed above, the critical property could change depending on the material and the end use.

It is particularly necessary to know the age of the prepreg if it is to be used under field conditions (such as on a base or on a carrier) to effect repairs to a composite structure. In such situations, the prepreg is used infrequently and long periods of storage are possible. Exhaustive testing of the prepreg prior to use is not feasible and an overage indicator would be most useful. A simple overage indicator would obviously have the greatest advantage for field use whereas a more complex, rigorous test would be more appropriate for in-plant use.

This report describes aging studies that were carried out on one product - Hercules 3501-6/AS graphite epoxy prepreg. Several methods that successfully track the age of the prepreg and which can be used as overage indicators are described. These are dielectric analysis (DA), dynamic mechanical analysis (DMA), and a time-temperature integrating indicator (TTW). The latter is a simple device which is carried with the prepreg and should be most useful for field use as suggested above. The other two methods, while simple to use, require the use of relatively sophisticated and expensive analytical equipment.

During the aging studies reported previously[1,2] and in this report, it was noted that humidity in the aging environment affected the relative reaction of the prepreg resin mix as observed by isothermal DA experiments. Therefore a mini study was undertaken to determine the effect of moisture from a humid environment on the aging characteristics and the reaction rate of 3501-6/AS prepreg.

Much work has been done to study the effects of humidity on fully cured graphite composites, however very little has been done to determine the effects of moisture on uncured graphite prepregs. The graphite-epoxy composites have shown a loss of strength after exposure to high humidity conditions followed by a thermal spike (a sharp increase in temperature followed by a sharp decrease used to simulate aircraft take-off conditions).[3] While it is generally believed that graphite-epoxy prepregs are also affected by moisture from humidity exposure, a literature search has revealed only a little information on the subject.[4] Humidity effects would be of concern where the prepreg is likely to be used in a non-controlled environment.

Experiments were performed in which the prepreg was aged under humid and dry conditions at several temperatures. At periodic intervals, DA was used to study the reactivity of the prepreg resin at several temperatures. Liquid chromatography was also used to study the changes caused by aging in a humid environment.

It should be noted that the present work reported in this document is a continuation of the effort reported earlier and therefore should be read in conjunction with that report.[1]

## 2. SUMMARY

The method used in this study was to determine (for a given material) that critical property which is the first to deteriorate when the material is aged in shipping, storage, and handling. Various techniques are then used to track the aging of the prepreg under diverse storage conditions. The results obtained are correlated to the deterioration in the critical property. Thus each technique provides a number (or value) which is then used as a decision point to reject that lot of material as having exhausted its useful life.

Under the present contract the material examined was 3501-6/AS graphite prepreg supplied by Hercules, Inc., Magna, Utah. It was determined from our aging studies that the critical property that first deteriorates on aging is tack. This was also confirmed by the supplier.

During the course of the study, samples of the 3501-6/AS prepreg were obtained from the supplier. The prepreg was subjected to several aging conditions.

Data from the following conditions were presented in the previous reports[1,2]:

- Freezer storage (-4°F)
- Room ambient (78°F, 62% RH)
- 120°F

- 120°F, 95% RH
- Intermittent exposure from freezer to room ambient.

Data from the following conditions are presented in this report:

- Intermittent exposure from freezer to 120°F, 80% RH
- Laboratory ambient aging of prepreg aged one year in the freezer
- Room temperature (74°F) and 80% RH
- 104°F
- 104°F and 90% RH
- 160°F, 40% RH.

During these aging periods, the following tests were performed:

Tests of Age Indicators

- Time Temperature Integrator: Several types of indicators (from two suppliers) were obtained and exposed to the same aging conditions as the prepreg. The purpose was to see if under diverse aging conditions, the devices would track the age of the prepreg and would provide a value which would correlate with the loss of the critical property.

- Dielectric Analysis (DA): During the aging, at periodic intervals, measurements were made on the prepreg using an automatic dielectrometer. The measurements were made under dynamic temperature conditions to obtain the temperature of the relaxation peak in dissipation factor, and under isothermal conditions to obtain the isothermal time to peak in dissipation factor.

- Dynamic Mechanical Analysis (DMA): At periodic intervals during the aging, the temperature of the relative damping peak was obtained using a dynamic mechanical analyzer (DuPont Model 980).

- Differential Scanning Calorimetry (DSC): While recognizing that DSC should theoretically be useful as an overage indicator, it was not studied in this period because of the negative results obtained during the previous period.[1]

## Physical Properties of the Prepreg

During the aging study, at periodic intervals the resin flow and prepreg tack were measured.

## Mechanical Properties of Laminates

Periodically, laminates were press molded from the aged prepreg. The flexural strength, flexural modulus, and interlaminar shear strengths of the laminates were measured. This was done for all of the aging conditions studied in the previous period and for two conditions defined in this report. The measured mechanical properties do not show any degradation till well beyond the useful life of the prepreg. Therefore, for reasons of economy, mechanical properties were not measured during the rest of the studies.

## Effect of Moisture on Reaction Rate of the Prepreg

The effect of moisture on the curing reaction of Hercules 3501-6/AS graphite-epoxy prepreg was investigated. Test samples of prepreg were aged at 120°F, 80% relative humidity (RH); 100°C, 80% RH; and room temperature, 90% RH, while control samples were aged under identical temperature conditions but with negligible humidity. Determination of the amounts of moisture absorbed and desorbed from the samples were accomplished gravimetrically. Dielectric analysis was used to monitor the relative reaction rates and overall activation energies of the prepreg after various aging periods. Liquid chromatography (LC) measurements were used to follow chemical changes taking place in the prepreg during aging in humid and dry environments. Peaks associated with the principal monomers and a reaction product were identified and were used to characterize the difference between humid and dry aging.

# 3. EXPERIMENTAL

## 3.1 AGING STUDIES

### 3.1.1 Materials

The aging behavior of only one material was investigated in this study. This is the Hercules 3501-6/AS prepreg. It consists of unidirectional "A" type graphite fiber which is impregnated (without solvent) with an epoxy resin mixture which is only slightly B-staged. While the supplier will not disclose the precise constituents of the matrix, this much is known: It consists of three epoxides of which one the principal is tetraglycidyl methylene dianiline (TGMDA). The curing agent is diaminodiphenyl sulfone (DDS) and the catalyst is a $BF_3$ complex.

During the course of the study, four batches of prepreg were obtained from the supplier. Normal shipping channels were used and no special handling was used. Hercules was asked to activate and include several TTWs with each shipment. For the purposes of this report, the four batches obtained are labeled F, FN, FA and MF. Table 1 presents information on the four batches of material as given by the supplier. Note the resin contents of the four batches. FA is a special low resin content grade and was obtained in April 1978 to verify what effect the lower resin content might have on our studies. Batches F and FN were used in the studies reported earlier[1], while FA and MF batches were used in the studies reported herein.

TABLE 1

BATCHES OF 3501-6/AS PREPREG USED IN THIS STUDY

| Batch ID | Hercules Lot and Spool No. | Resin Content (%) |
|---|---|---|
| F | 597<br>4H | 42 |
| FN | 612<br>3C | 41 |
| FA | 791<br>2A | 35 |
| MF | 1041<br>2B | 43 |

### 3.1.2 Time-Temperature Integrators

These integrators are devices that integrate the time and temperature to which they have been exposed and display the integrated product as a color change on a numbered strip. The change in color may then be correlated to the end of the useful life of the prepreg or in general to any material that ages during shipping and storage.

Two types of integrators were investigated in the course of this study. They are (a) Time/Temperature Watch (TTW) supplied by the Info-Chem Div. of Akzona, Inc., and (b) Monitormark made by the 3M Co.

3.1.2.1 Time-Temperature Watch. In the previous report[1] it was concluded that a Type 33 TTW was appropriate for use as an overage indicator for 3501-6/AS prepreg. This conclusion was further tested under more diverse aging conditions and the results are reported here. The different types of TTWs, the process of selecting the Type 33, their aging behavior and the effect of humidity on the aging behavior of the TTWs has been fully discussed.[1]

3.1.2.2 Monitormarks. 3M Company's Monitormarks serve the same function as the TTW, i.e., to monitor the time and temperature exposure of the product. They work somewhat differently in that each Monitormark has an initiation temperature below which it will show no change. The color change on the Monitormark advances up the scale (logarithmic from 0-5 units) when the initiation temperature is passed. Commercial Monitormarks are designed to run out in either 2 days or 15 days of exposure to temperatures above the initiation temperature.

Monitormarks capable of operating for more than 30 days were obtained from 3M Co. We selected three initiation temperatures, 19°F, 41°F and 59°F and the Monitormarks were labeled T7, 5R and 15Q, respectively. Based on the curves supplied by the manufacturer, we felt that no single Monitormark would be able to follow the aging of the prepreg adequately. In spite of that, the Monitormarks were evaluated

at several aging conditions. The effect of humidity in the aging environment on the Monitormark readings was also evaluated.

### 3.1.3 Dielectric Analysis (DA)

An automatic dielectrometer was used to monitor the aging of the prepreg and define an overage condition for the prepreg. The procedure and techniques used were described in detail in References 1 and 2. In brief, measurements are made in the temperature variant mode at a rate of 10°C/min and 1 kHz frequency. The sample used consists of 1 ply of prepreg (dried in a desiccator for at least 2 hrs) under 1 ply of 1 mil thick polyimide film and the temperature of the peak in dissipation factor is measured. It increases with prepreg age.

### 3.1.4 Dynamic Mechanical Analysis (DMA)

A DuPont Instruments, 980 Dynamic Mechanical Analyzer was used to measure the change in prepreg age as described in detail in References 1 and 3. In brief, a 1" x 1/2" sample of prepreg is cut, dried in a desiccator for a minimum of 2 hrs and then placed in the clamps of the DMA. The DMA is then cooled to -20°C after which it is heated at a programmed rate of 10°C/min. As the prepreg heats up it undergoes a transition which results in a peak in the relative damping curve. The temperature of this peak was successfully used to characterize the age of the prepreg. As the prepreg ages, the temperature of the peak in relative damping increases.

### 3.1.5 Prepreg Physical Properties

Physical properties of the prepreg measured during the aging studies were tack and resin flow.

3.1.5.1 Prepreg Tack. Prepreg tack is its ability to adhere to a substrate or to itself. No good tack test is available because to an extent, the property is subjective and depends on the end use. Pieces of prepreg being laid flat would require minimal tack; complex shapes

and vertical layup would require a great deal of tack. A prepreg is tacky when at the ambient or use temperature the resin system is above its glass transition temperature (Tg). Then, when some reactions take place during storage or aging, increasingly larger molecular weight species are formed and the Tg of the prepreg increases above the ambient or use condition and the prepreg then loses its tack. Thus tack is influenced by: (1) Tg of the prepreg, (2) ambient temperature - increasing ambient temperature will increase tack, (3) humidity - increasing humidity will increase tack if the resin picks up any moisture, (4) resin content, and (5) test parameters.

Since the prepreg was supplied by Hercules, their test procedure was used to measure its tack. It is a go/no go test with the prepreg either passing or failing. The test is specified in Hercules, Inc. Graphite Composite Testing Procedures HD-SG-2-6006C, Section 5.4, and was performed at ambient conditions.

3.1.5.2 Resin Flow. Resin flow was determined by a press laminating procedure as detailed in Hercules Testing Procedures HD-SG-2-6006C, Section 5.3.1. (Note: Two tests were performed for resin flow and prepreg tack for each sample as called for in the test procedures.)

### 3.1.6 Laminate Properties

Selected laminate properties were measured to determine the changes taking place in them as the prepreg was aged.

Unidirectional laminates were press molded in a matched-metal mold which gave a laminate thickness of approximately 0.080". The mold was prepared as detailed in Hercules Test Procedure HD-SG-2-6005C, Section 5.1.1. Sixteen plies of prepreg were used to yield a cured nominal ply thickness of 0.005". The cure schedule used, similar to the autoclave cure schedule given in the Hercules Data Book for 3501-6/AS prepreg, is as follows:

1. Insert mold and prepreg into cold press and apply contact pressure.
2. Heat press at a rate of 20°F every 10 mins to 360°F + 5°F.
3. Apply 85 $\pm$ 5 psi when the temperature reaches 250°F.
4. Hold at 360°F for 120 + 15, -0 mins.
5. Cool to less than 150°F over 1 hr period before removing mold from press.

All laminate test specimens were cut from the panel and tested according to Hercules, Inc. Test Procedure HD-SG-2-6002C: - Cutting was done according to Section 5. Resin contents were obtained according to Section 6.2.2 (for A type fiber). Flexural strength and modulus were measured at room temperature according to Section 7.1, and the short beam shear strength at room temperature according to Section 7.3.

## 3.2 EFFECT OF MOISTURE ON THE RELATIVE REACTION RATE OF THE PREPREG

Samples of Hercules 3501-6/AS prepreg from the MF batch were exposed to $K_2Cr_2O_7$ (sat.) humidity bath (∿90% relative humidity) at room temperature; 80% relative humidity at 120°F (49°C) and 100°F (38°C) in a Blue M Humidaire oven. These humidities were arbitrarily chosen to produce simulated adverse environmental conditions. Control samples were exposed to identical temperatures in a forced-air oven and room temperature control samples were placed in a drybox for aging. At periodic intervals, samples were desiccated to remove any free water which could interfere with the dielectric analysis. Two hours were found to be adequate drying time. Undesiccated samples ("wet" samples) were also run to determine whether the "free" water in the sample would alter the results in any way.

Dielectric analysis was performed to study the reactivity of the resin in the prepreg with Tetrahedron's Audrey II (Automatic Dielectrometer), Di/An 300 (heated press), and SR-300 (3-channel scanning recorder). Samples, consisting of two layers of prepreg under one layer of 181 fiberglass and one layer of 1 mil polyimide film in a small aluminum sample dish were tested at 160, 170, 180, 190, 200°C at 1 kHz. By

presetting the Di/An test cell 5°C above the desired temperature prior to inserting the sample (to compensate for temperature loss during sample placement), isothermal conditions (± 1°C) could be reached in less than 1 min. During the isothermal run, the dissipation factor (tan $\delta$) was measured continuously as a function of time and frequency. The dissipation factor has a low value initially, but as the reaction proceeds, it begins to increase in value, eventually displaying a maximum, after which it decreases. These frequency dependent tan $\delta$ peaks are associated with gelation of the resin and therefore, the time to peak in tan $\delta$ at a given frequency is an inverse measure of the relative reaction rate.[(5,6)] Since lesser times to tan $\delta$ peaks result for faster reactions, the peaks at high temperatures will occur sooner than those at lower temperatures as shown in Figure 1 for unaged 3501-6/AS prepreg. It was experimentally observed that the 1 kHz frequency peak in tan $\delta$ occurred at the time of resin gelation. Therefore, 1 kHz was the frequency used for these analyses. A plot of log (time of tan $\delta$ peak) vs. the reciprocal of the absolute temperature will result in a straight line which is an Arrhenius plot for the reaction. The activation energy is obtained from the slope of the line.

Figure 2 shows the Arrhenius plot for unaged 3501-6/AS prepreg at measurement frequency of 1 kHz.

Regression analysis was used on the data to fit the best line to obtain the Arrhenius plots. The activation energy, determined from the slope of the regression line by multiplying it by the gas constant, R (1.987 cal/mole °K), is 13.5 Kcal/mole. Figure 2 also shows that the variation in the data obtained using dielectrometry is within ± 1 min.

The amounts of moisture gained by the prepreg during aging in the humidity chambers and lost during desiccation were determined gravimetrically. In addition to that, some moisture content analyses were done with a DuPont 902 Moisture Evolution Analyzer. This instrument contains a $P_2O_5$ coated electrochemical cell. Upon contact with moisture, the $P_2O_5$ is hydrolyzed to phosphoric acid. The phosphoric acid is then electrolyzed back to $P_2O_5$ and the current required is automatically converted and read out as micrograms of water. However, problems were

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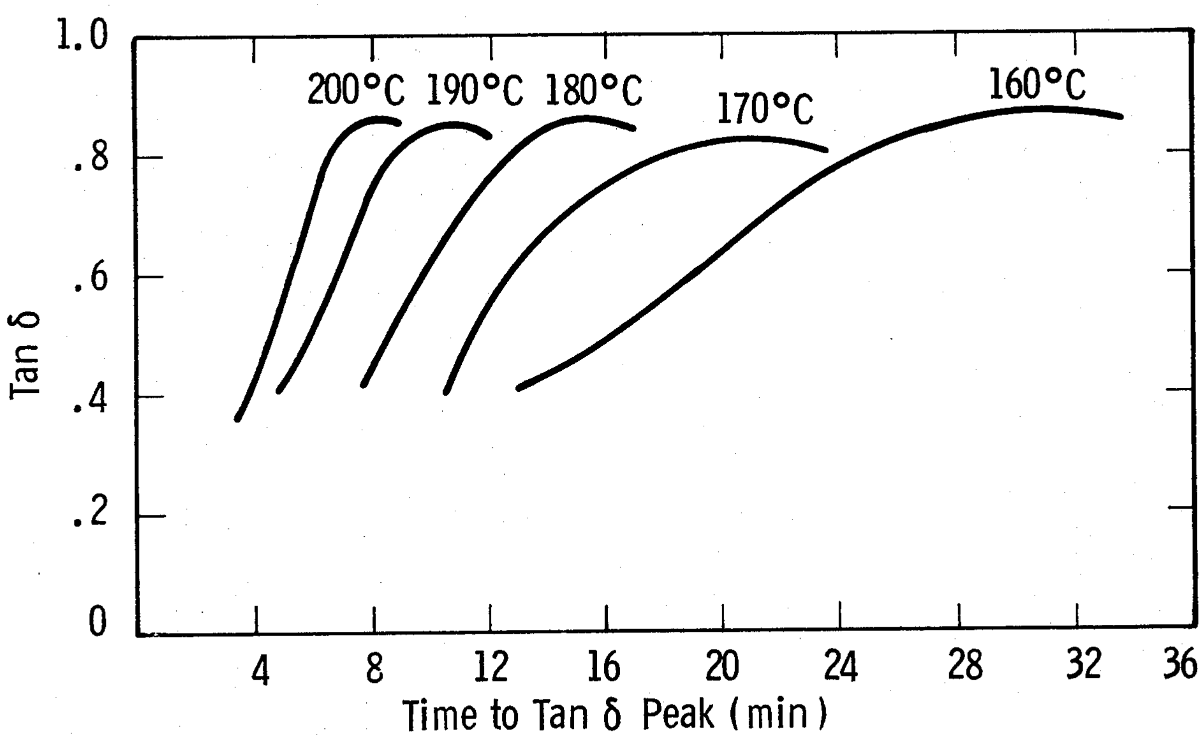


Fig. 1 — Peaks in tan δ at several temperatures during isothermal experiments at a frequency of 1 kHz with 3501-6/AS graphite epoxy prepreg

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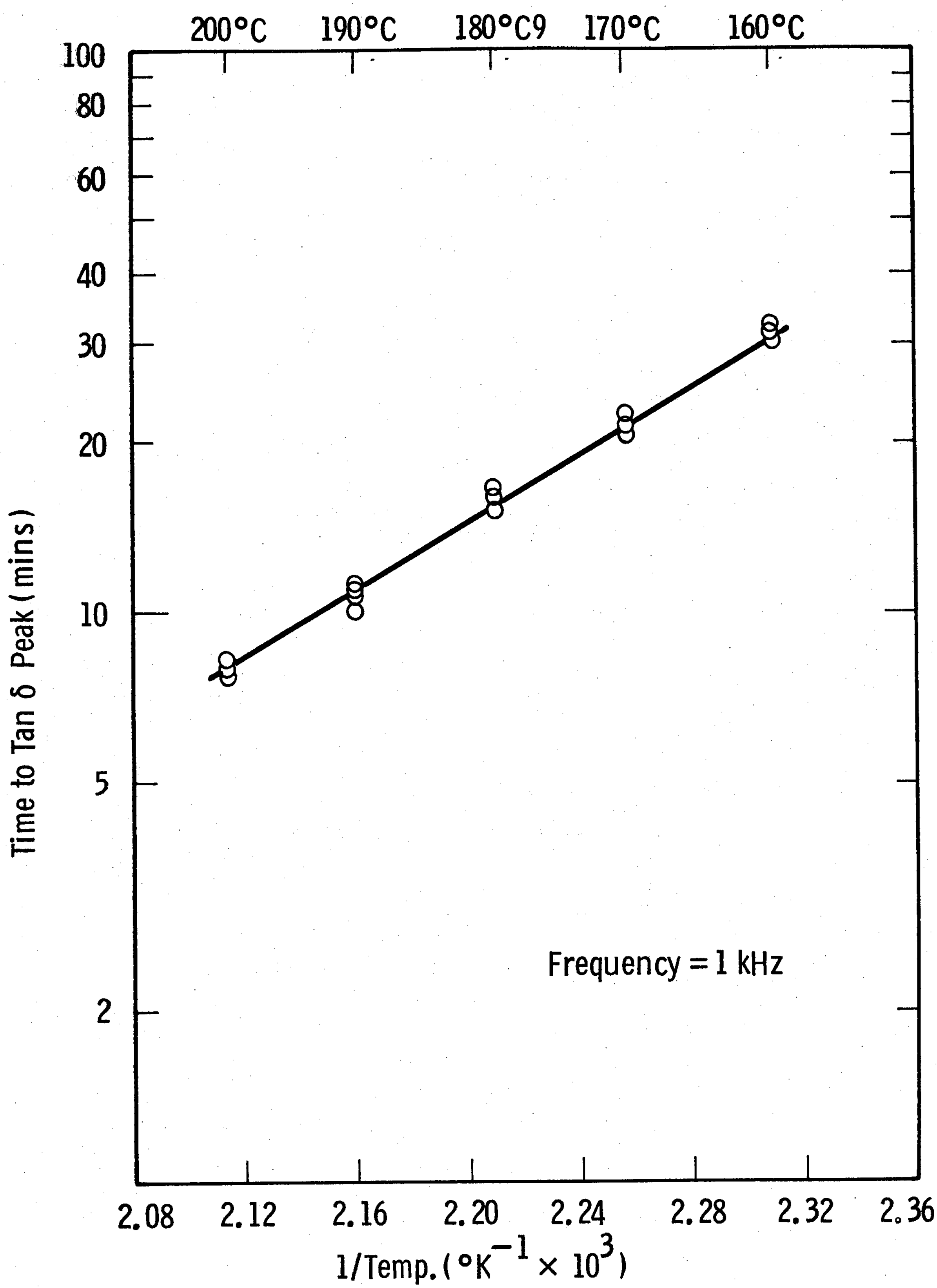


Fig. 2 — Arrhenius plot for the reaction of unaged prepreg

encountered with contamination of the $P_2O_5$ electrolytic cell, the heart of the instrument. Resin flow was also determined using the procedure described in Section 3.1.5.2.

Liquid chromatography was used to investigate the effect of moisture on the curing reaction of 3501-6/AS prepreg. The chromatography was performed during the 120°F, 80% RH and 120°F, dry oven aging study, according to methods developed by G. L. Hagnauer.[1,7] The chromatographic analysis was performed using a 25 cm by 4.6 mm I.D. stainless steel column packed with 10 micron silica gel. The solvent which was used elute the sample from the column was varied from 40% dioxane in iso-octane to 100% dioxane in 20 min. The solvent flow rate was maintained at 1.0 ml/min. Three components corresponding to TGMDA (N,N,N´,N´-tetraglycidyl methylene dianiline), DDS (diaminodiphenyl sulfone) and the principal reaction product were identified. Peak heights, which are proportional to concentration, were measured for the various components and an absolute response was calculated in terms of absorbance units per mg at 280 nm. Thus, the reduction in the concentration of the monomers (TGMDA and DDS) during the aging of the prepreg can be measured.

## 4. AGING STUDIES ON 3501-6/AS PREPREG

Data from the aging studies are presented in graphical form. Error bars on the data points represent $\pm$ 1 (standard deviation). Data for the TTW does not have error bars because the readings were usually within one-half unit of each other and the reading accuracy is about the same in the present package configuration.

Aging studies reported previously[1] (see Section 2) will not be individually discussed here. However, the conclusions section summarizes all data from all aging studies whether performed previously or during this reporting period.

## 4.1 USEFUL LIFE OF THE PREPREG

During aging studies it was found that 3501-6/AS prepreg lost its tack before any other property suffered deterioration. Prepreg tack thus became the critical property for this prepreg as it was the first property to deteriorate with age. For purposes of this study, useful life of the prepreg was considered over when it had lost its tack. Tack was measured at ambient conditions according to the procedure outlined in Section 3.1.5.1.

## 4.2 INTERMITTENT EXPOSURE FROM THE FREEZER (-4°F) TO 120°F AND 80% RH

This study was performed using 35% resin content prepreg (FA batch) and was partly presented in the previous report.[(1)] The complete results are presented in Figures 3-6. Figures 3 and 4 present the TTW, DA and DMA data. The prepreg fails the tack test when the TTW Type 33 reading is 4.5, the dissipation factor peak temperature is 64°C and the relative damping peak temperature is about 30°C. Figure 5 shows that resin flow diminishes with prepreg age, consequently the resin content of laminates made from aged prepreg increases. The effect of this is shown in Figure 6. As the resin content increases to 30%, the flexural strength and shear strength increase to a maximum. Further increases in the resin content leads to diminishing values of strength and modulus, which is in accordance with results reported previously.[(1)]

## 4.3 AMBIENT AGING OF ONE YEAR OLD PREPREG

Some of the original F batch (42% resin content) prepreg which had been stored in the freezer for over one year was aged at ambient conditions which averaged 76°F and 60% RH during the test. The results are presented in Figures 7-10. Prepreg failed the tack test at a Type 33 reading of 4, DA reading of 64°C, and a DMA reading of 38°C. This happened after 21 days at room temperature. Comparison with ambient aging results of the F batch when freshly obtained shows only very slight degradation of the prepreg caused by storage in the freezer for one year. For the

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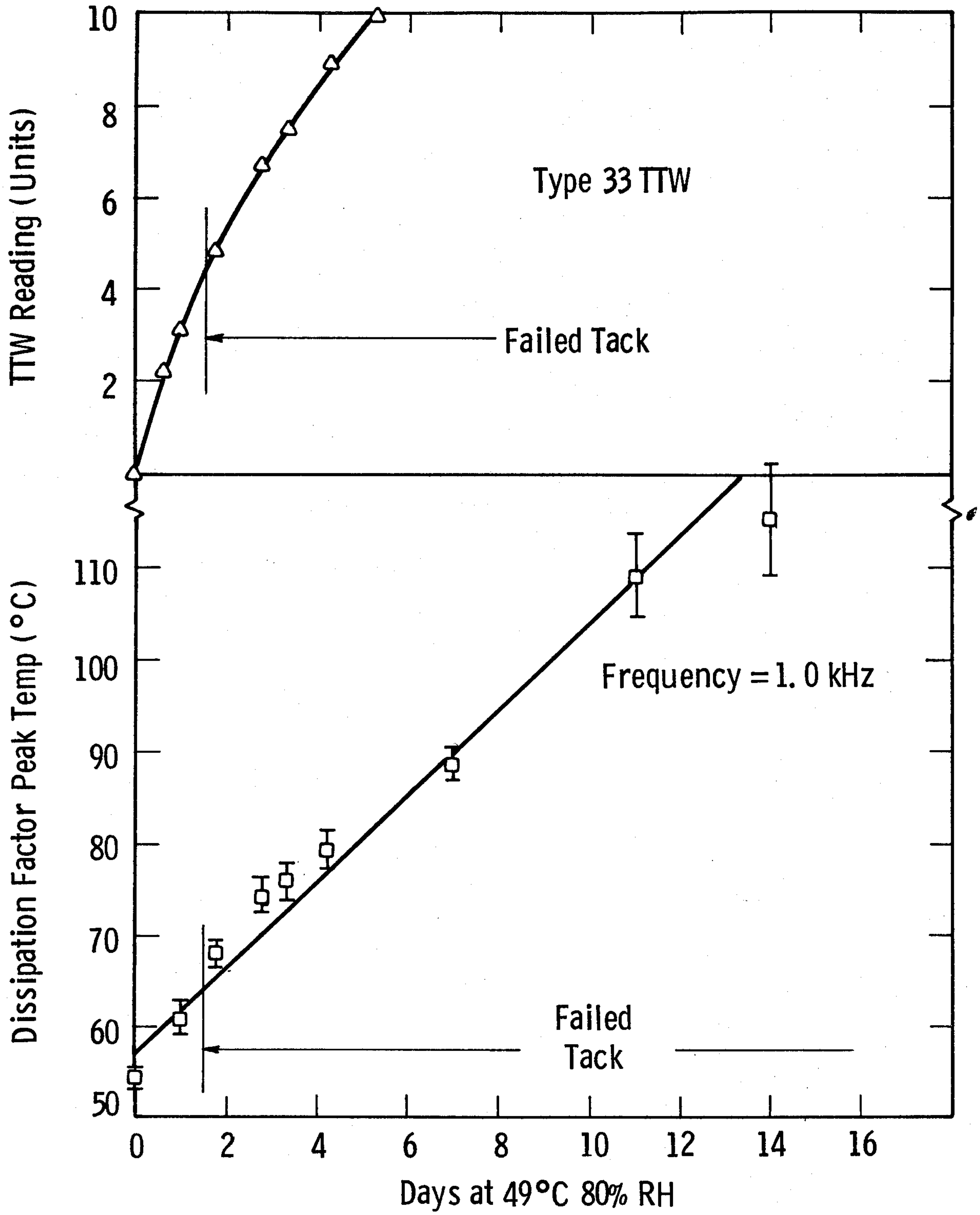


Fig. 3 — FA batch, 49°C 80% RH aging - dielectric analysis and TTW data. * Intermittent exposure from freezer (−20°C) to aging conditions

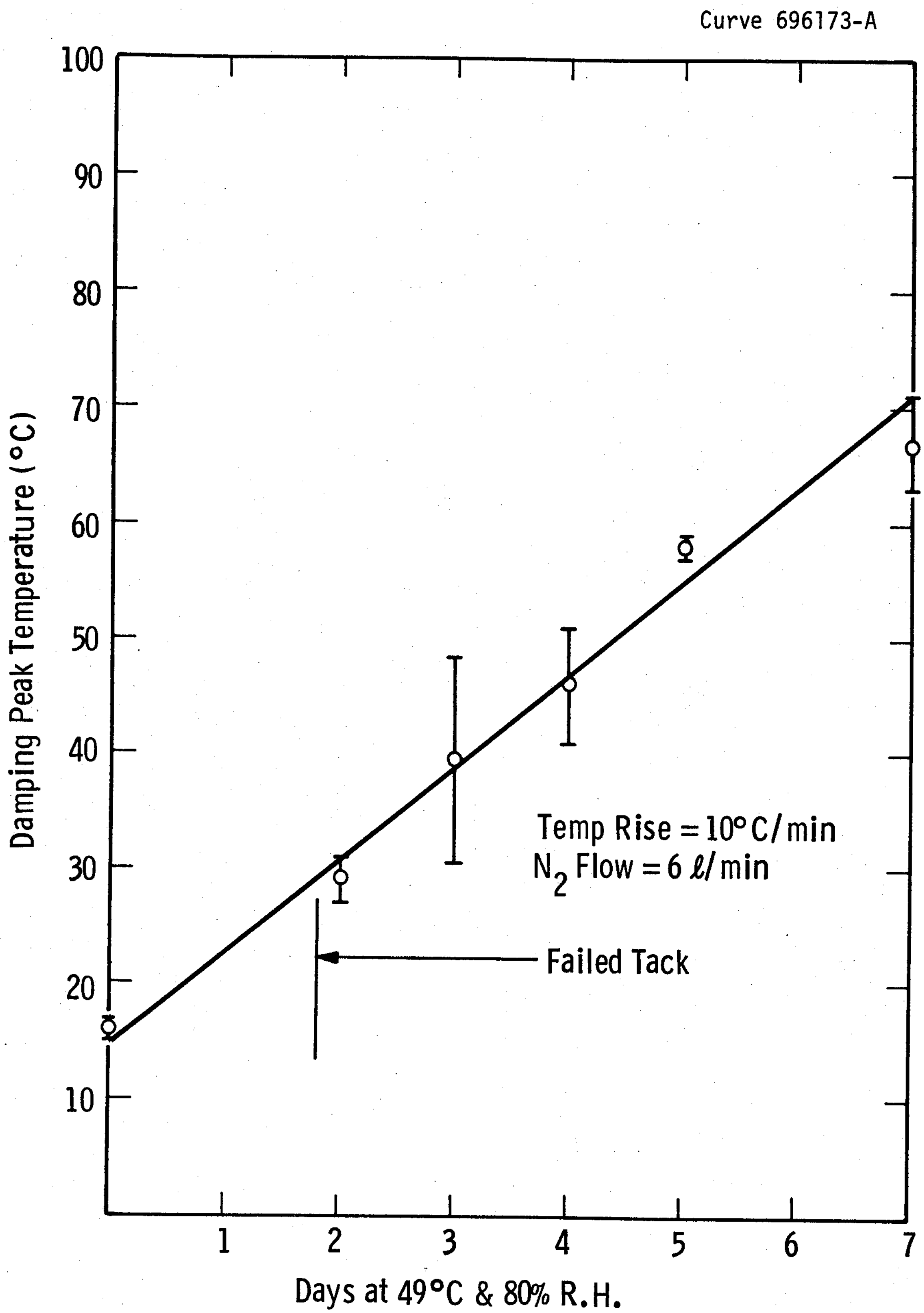


Fig. 4 — Intermittent exposure from freezer —20°C to 49°C & 80% R. H. — DMA data (FA batch)

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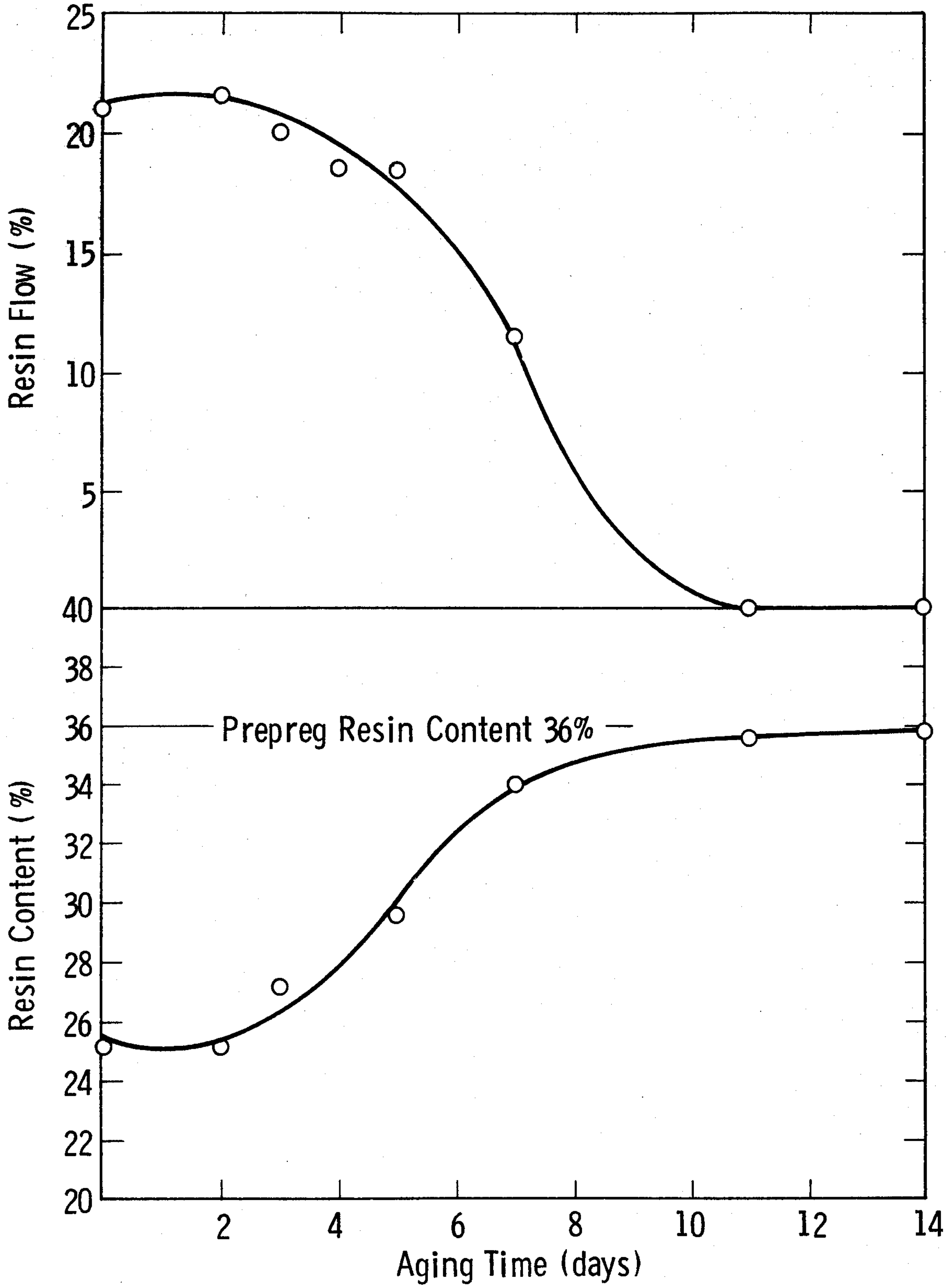


Fig. 5 — Intermittent exposure from −4°F to 120°F and R H. Resin content (by laminate digestion) data and resin flow data

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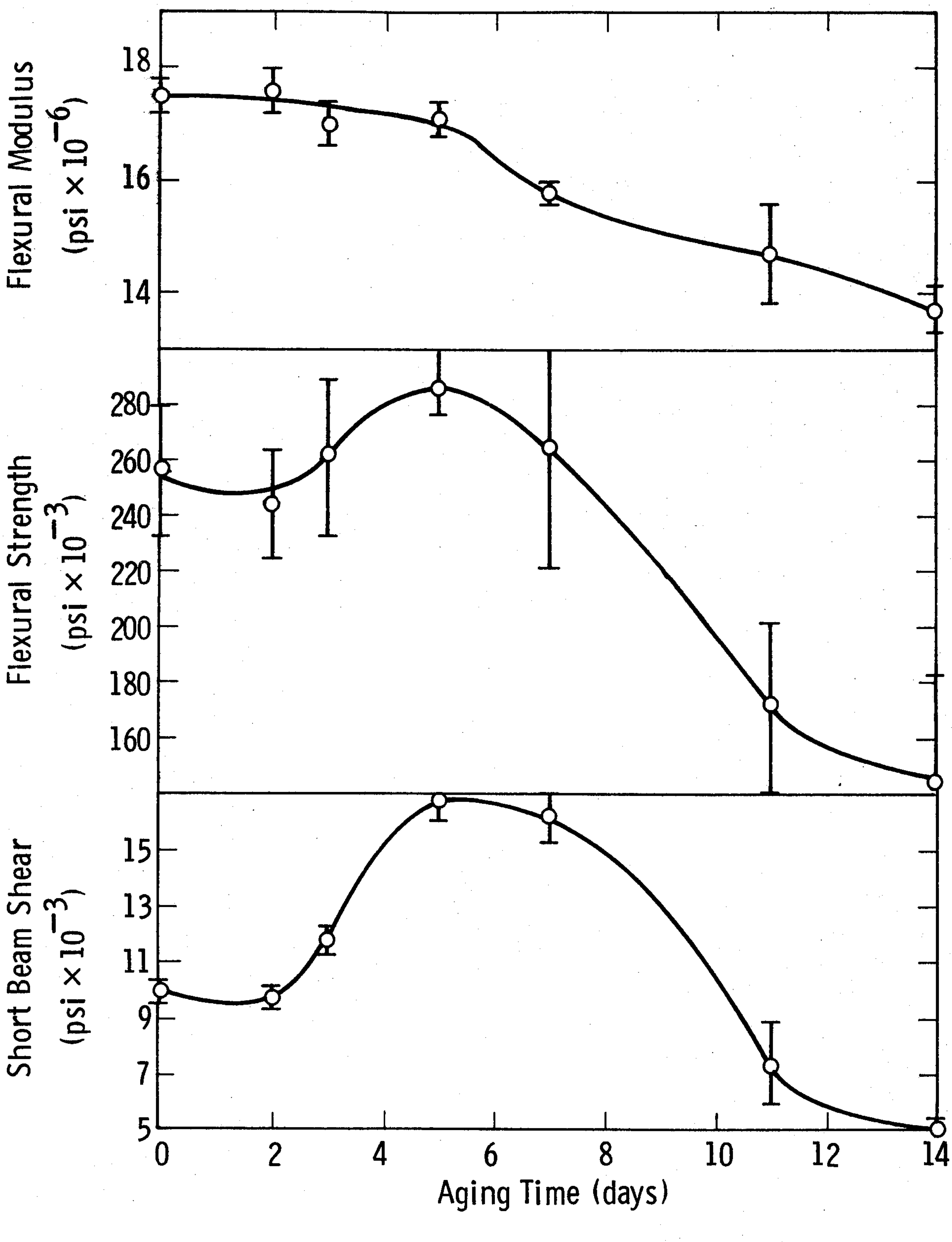


Fig. 6 — Intermittent exposure from −4°F to 120°F and R H. Mechanical test data FA batch

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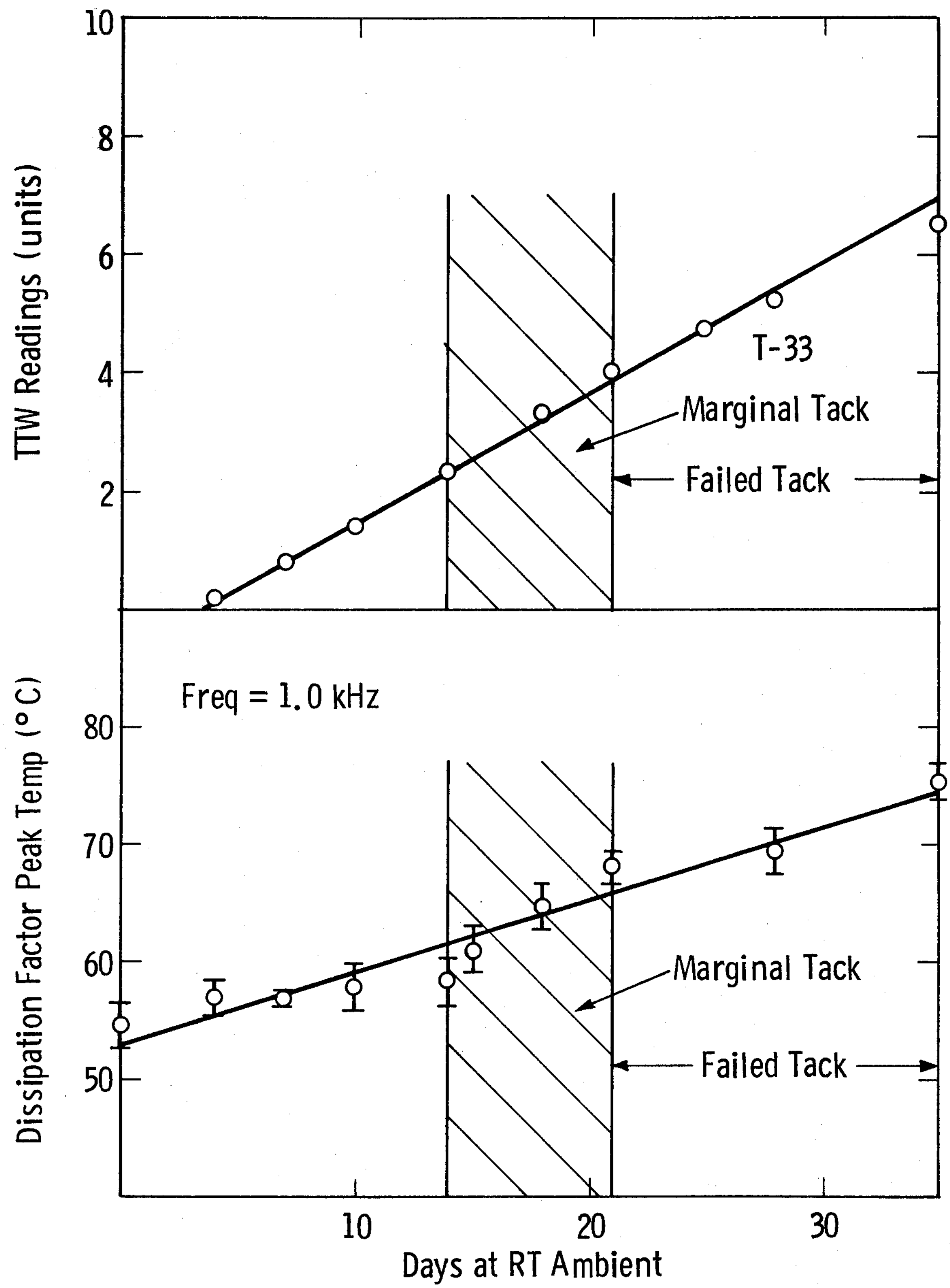


Fig. 7 —One year old prepreg with room temperature aging "F" batch. Dielectric analysis data and TTW data

Curve 715344-A

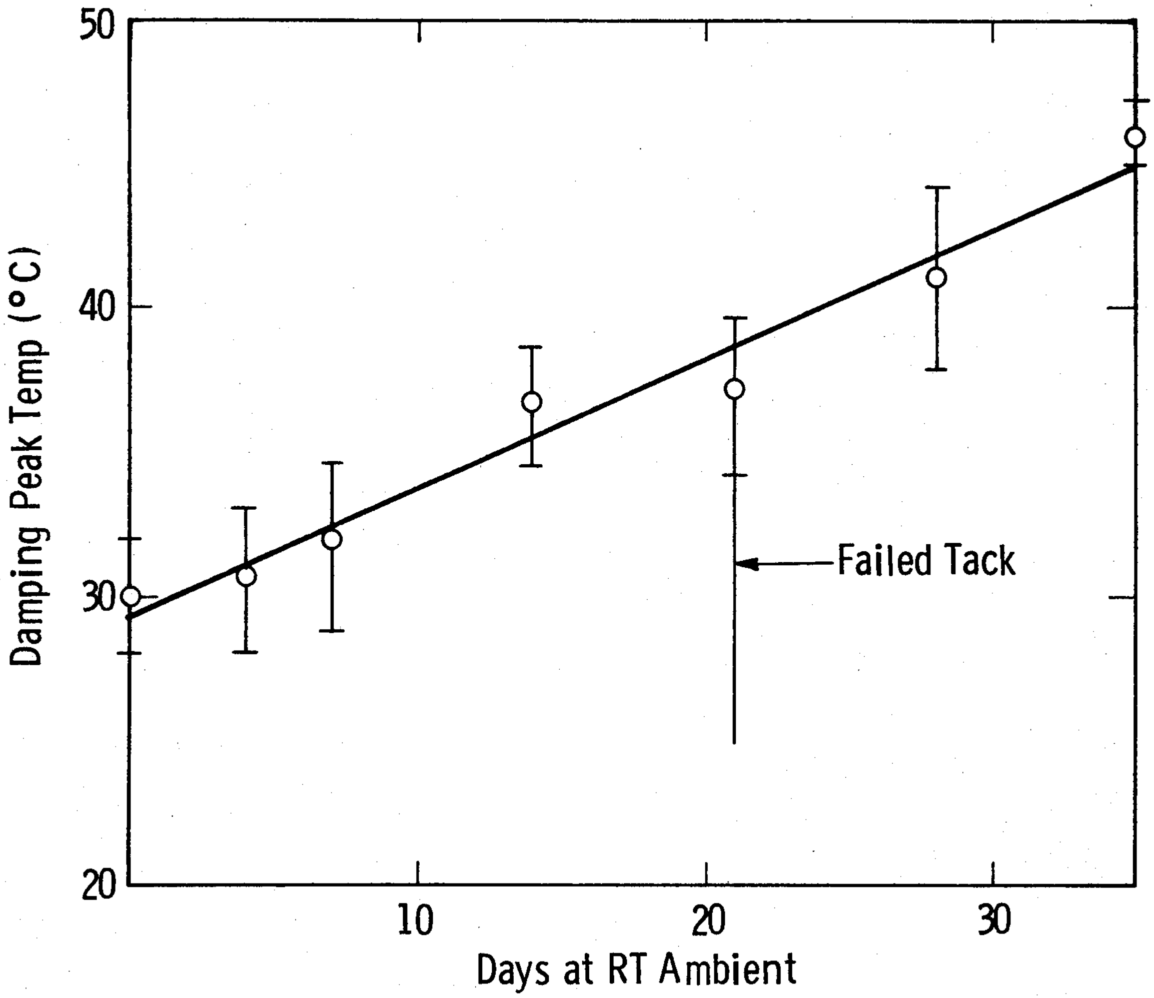


Fig. 8 — One year old prepreg with room temperature aging "F" batch. DMA data

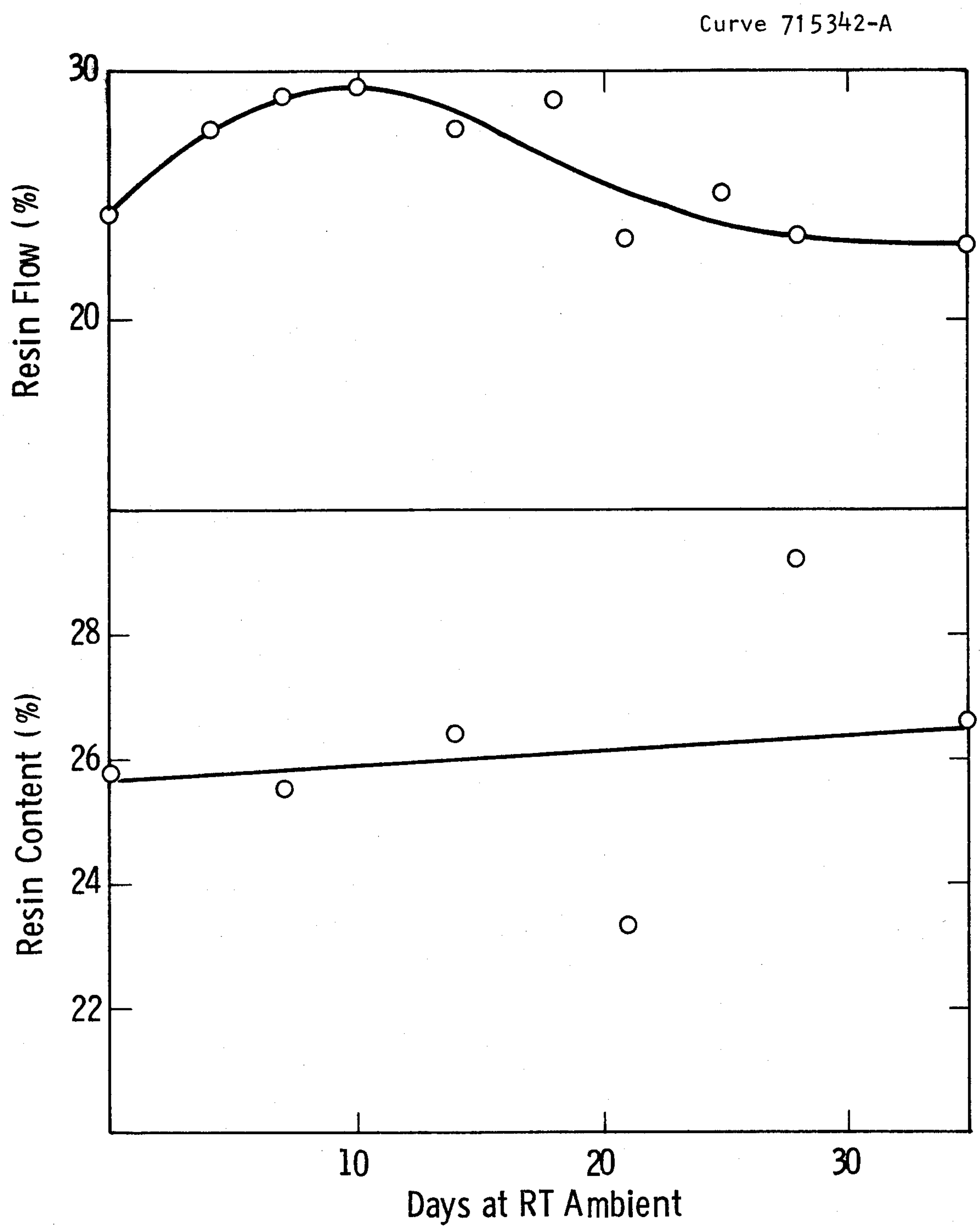


Fig. 9 — One year old prepreg with room temperature aging "F" batch. Resin content (by laminate digestion) data and resin flow data

Curve 715346-A

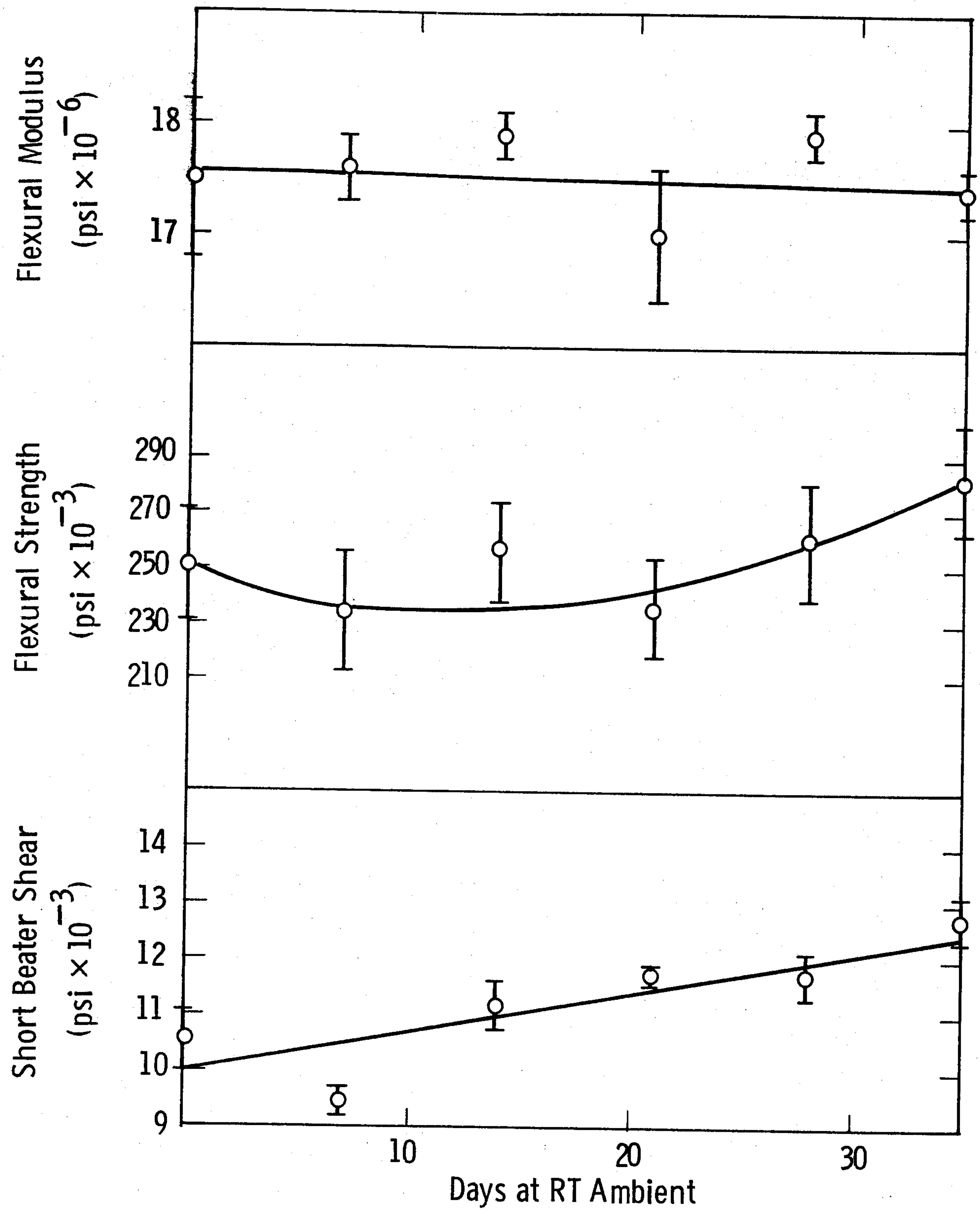


Fig. 10 — One year old prepreg with room temperature aging "F" batch. Mechanical test data

freshly obtained prepreg tack failure took place at 28 days with a TTW reading of 6 and the peak in dissipation factor occurred at a temperature of 64°C.[1] Figures 9 and 10 show that as the resin flow decreased with age, the resin content of the laminate increased slightly and therefore the mechanical properties of the laminate improved with age of the prepreg.

## 4.4 ROOM TEMPERATURE (AVERAGE 74°F) AND 80% RH AGING

This aging study was performed with the MF batch of prepreg which contains 42% resin content. The purpose of this condition was to verify the effect of high humidity at ambient temperatures on the TTW and the prepreg aging characteristics. As anticipated, the high humidity caused the indicated TTW color change to progress slower than when under dry conditions. This is shown in Figure 11 where the TTW had a reading of 4 when the prepreg lost its tack (its useful life). Under somewhat lower humidity conditions (62% RH)[1] the TTW reading was 5 when the prepreg useful life was considered over. Figure 11 also shows that using DA, the peak temperature in dissipation factor was 64°C at a frequency of 1 kHz at the end of the prepreg useful life. Figure 12 shows that resin flow declines very slightly during the aging study. The lower part of Figure 12 shows the isothermal DA data obtained at 180°C. The time to peak is an inverse measure of the relative reaction rate and the data indicate an initial reduction in the reaction rate followed by an increase. This type of effect was investigated in greater detail and is reported in Section 5. Figure 13 shows DMA data for this aging condition. Tack was marginal after 16 days at which point the temperature of the relative damping peak was 34°C. Loss of tack occurred after 26 days at which point the temperature of the relative damping peak was 44°C. This is much higher than that observed in any other aging study. It may be attributed to lack of machine calibration because this study was performed just after the DMA had been repaired.

Curve 716034-A

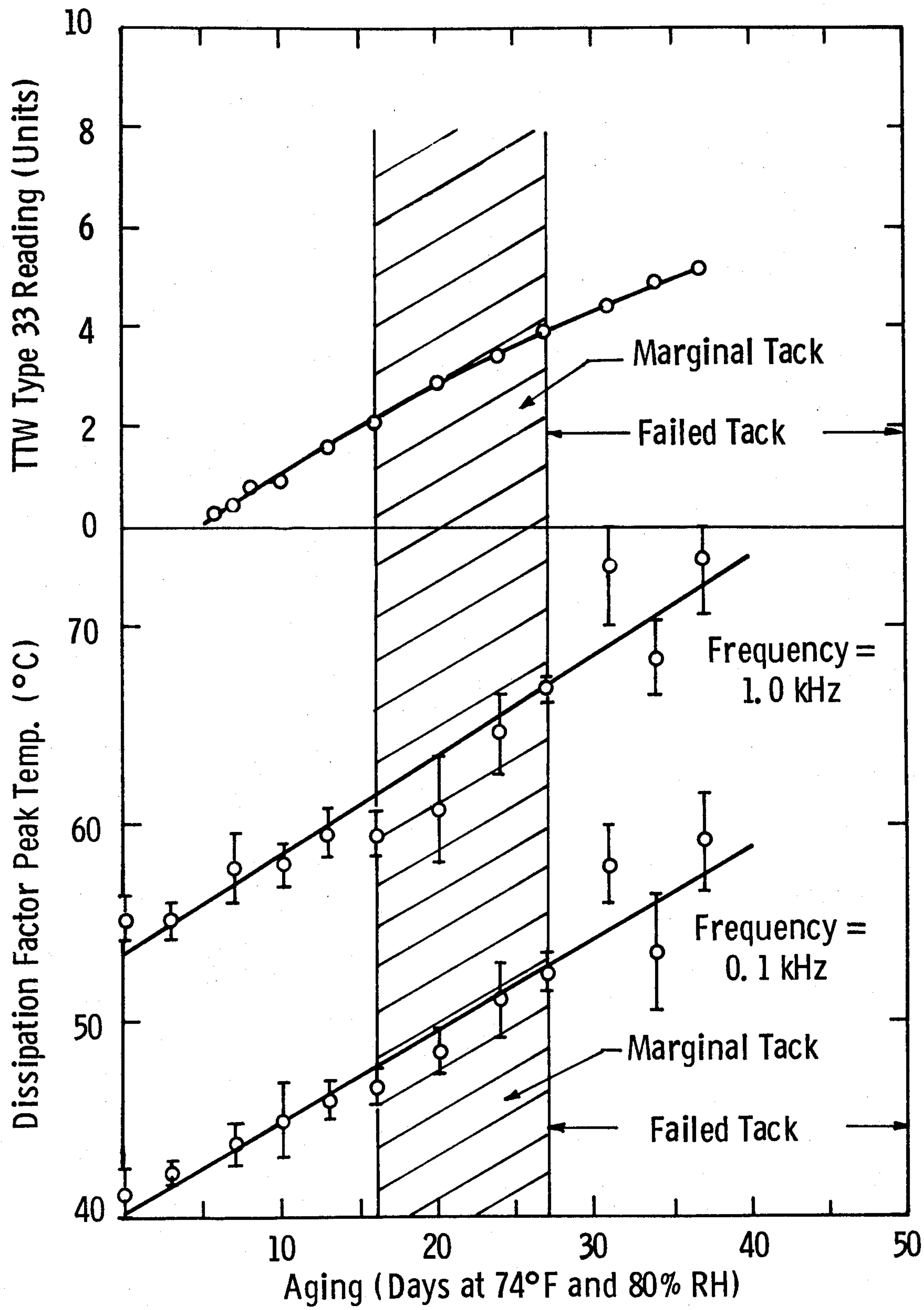


Fig. 11 – Aging at 74°F and 80% RH. Dielectric analysis and TTW data

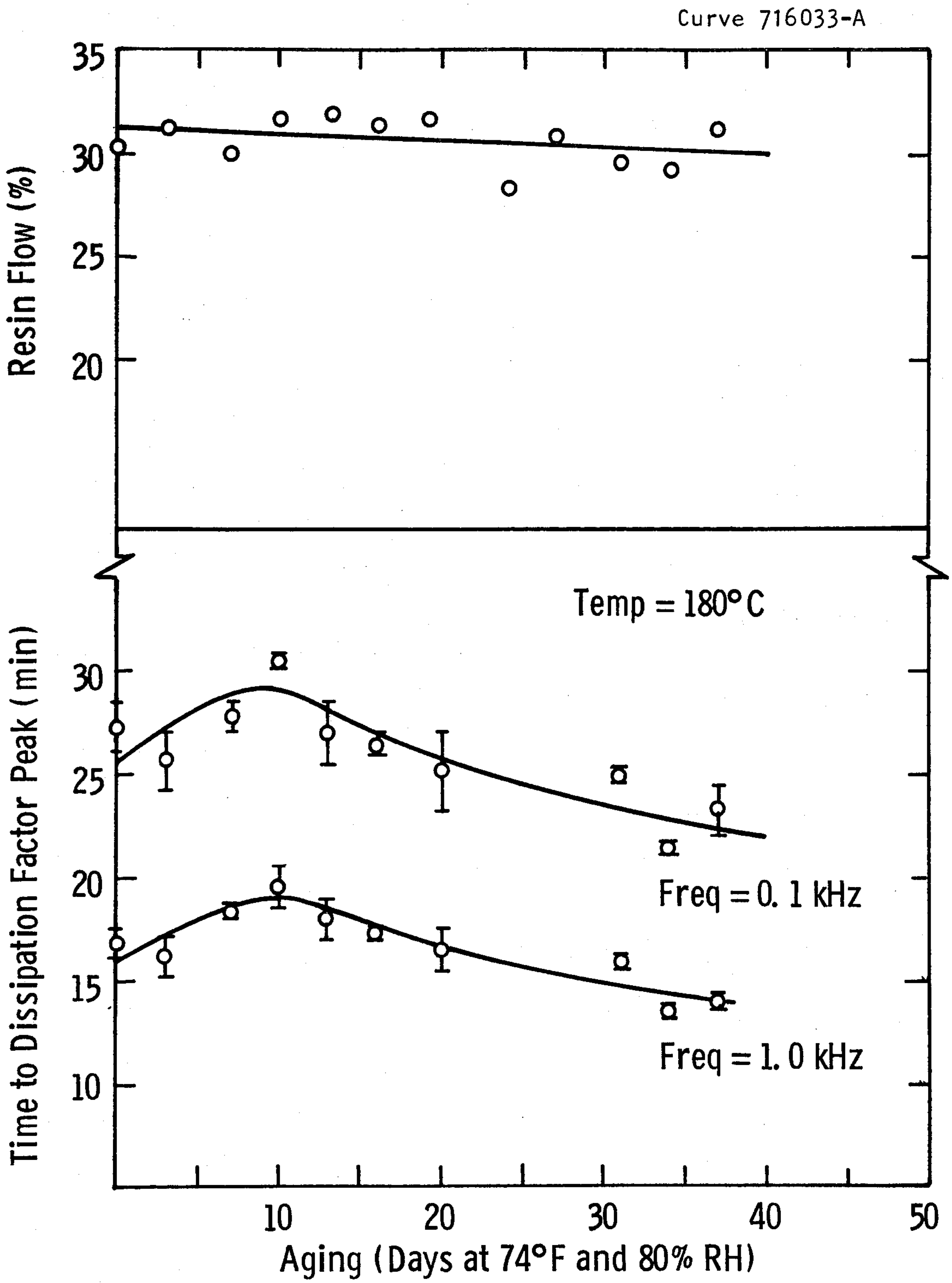


Fig. 12— Aging at 74°F and 80% RH. Resin flow and dielectric analysis data

Curve 716693-A

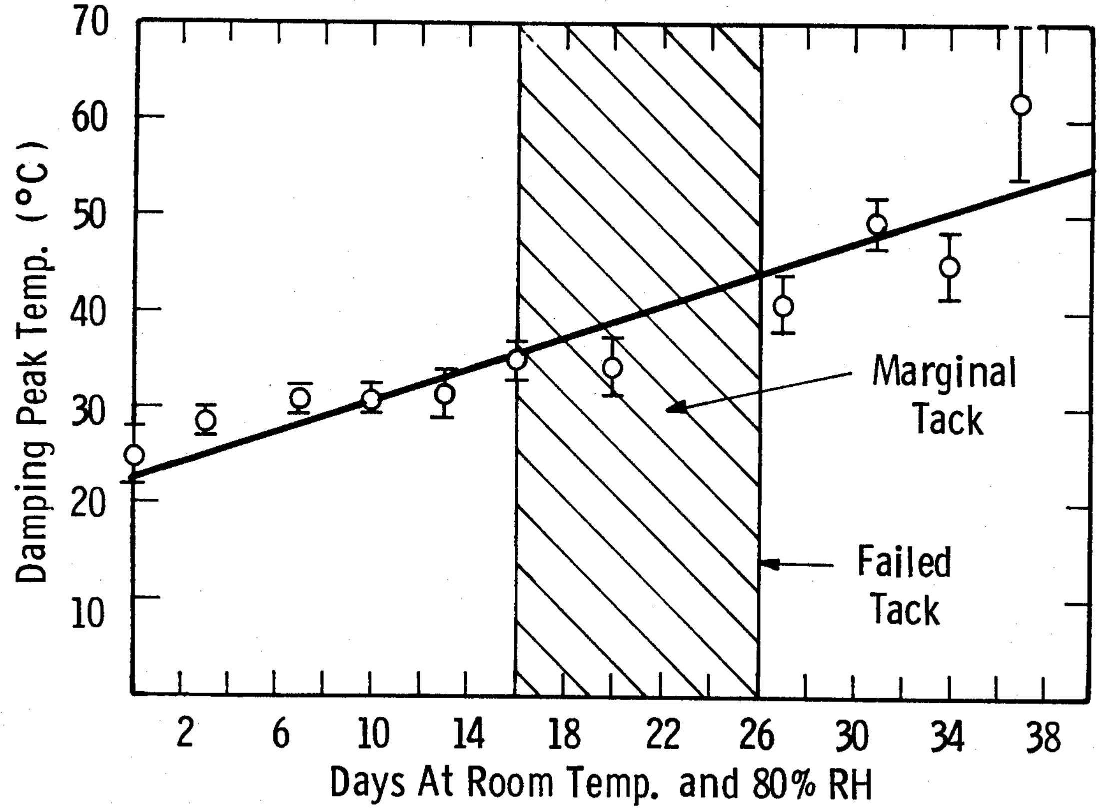


Fig. 13 — Aging at room temp, and 80% RH, MF batch, DMA data

4.5 160°F, 40% RH AGING

This condition is rather extreme and was selected to observe the behavior of the TTW at this extreme. As might be expected, deterioration of prepreg tack occurred within hours instead of days. The results, shown in Figures 14, 15 and 16, are in accordance with established overage conditions. Loss of tack occurs after 8 hrs at which point the Type 33 TTW reads 5. Using DA, temperature of the peak in dissipation factor at 1 kHz is 61°C. Using DMA, temperature of the peak in relative damping is at 34°C. Figure 16 shows the resin flow data at the top and DA isothermal 180°C data at the bottom. The expected gradual decline in value is exhibited by both sets of data.

4.6 104°F AND 104°F, 90% RH AGING

This study was carried out to provide more data for the TTW, Type 33 and the correlation of its readings to loss of prepreg tack. Loss of tack in both cases occurred on the fourth day at which point the TTW Type 33 showed a reading of 4 for the 90% RH condition and 6.5 for the dry condition.

4.7 STORAGE STABILITY OF TYPE 33 TTW

A set of the Type 33 TTWs were stored in a 120°F air circulating oven to verify their storage stability. Sets of three samples were withdrawn after one month, two months, four months and six months. They were then activated and allowed to run at 120°F while observations were made from time to time. The results are shown in Figure 17, with each data point being an average of three samples. The line marked "Unaged" is our base line compiled from previous work. It is seen that up to four months storage there was no change in the reactivity of the TTWs but the last set of data (after six months aging) does show a reduction in the reactivity. We have samples aging which will be tested after nine months and one year and will confirm whether this change is real.

Curve 716690-A

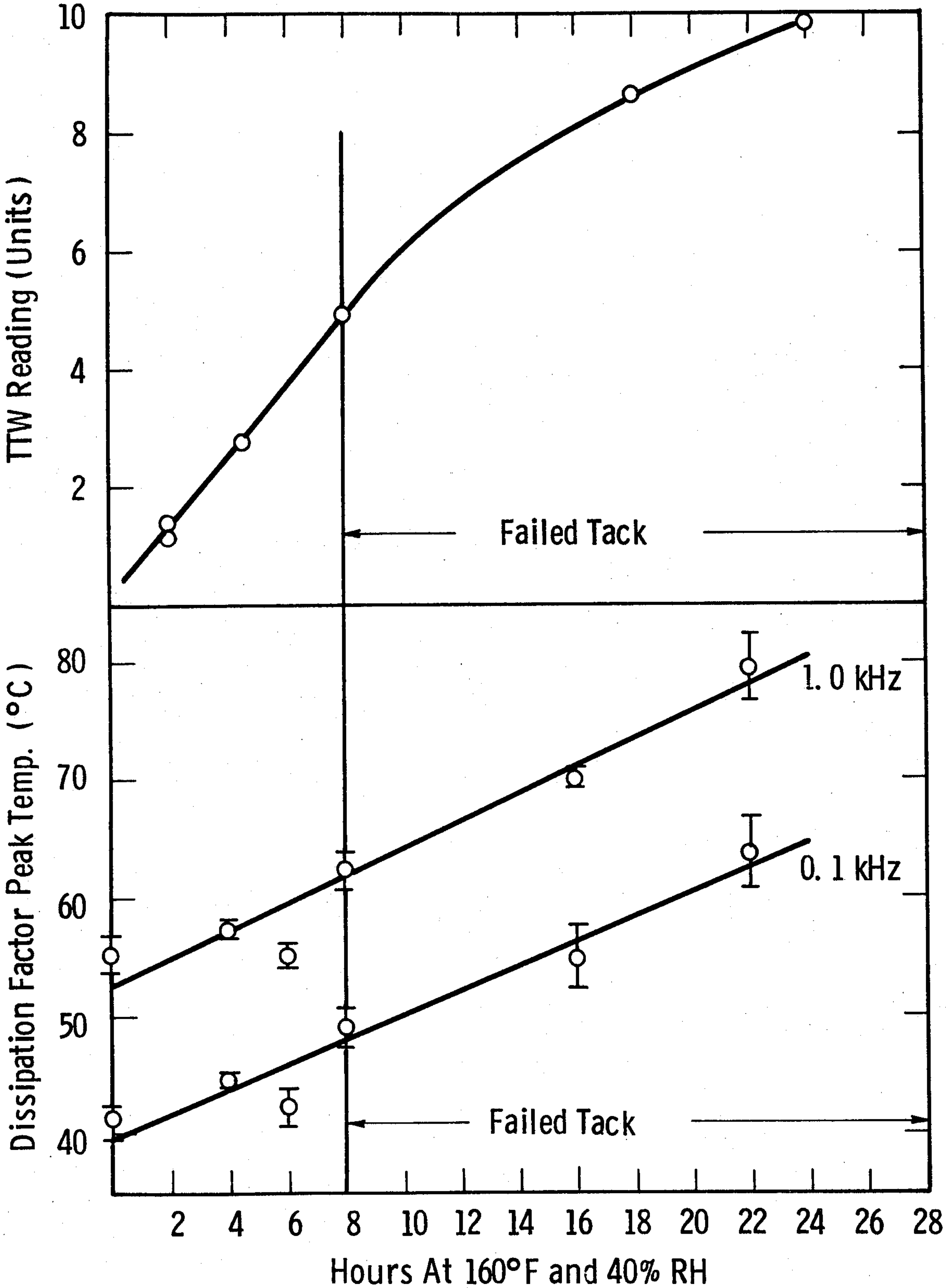


Fig. 14 — Aging at 160°F and 40% RH, MF batch, Dielectric analysis and TTW data

Curve 716692-A

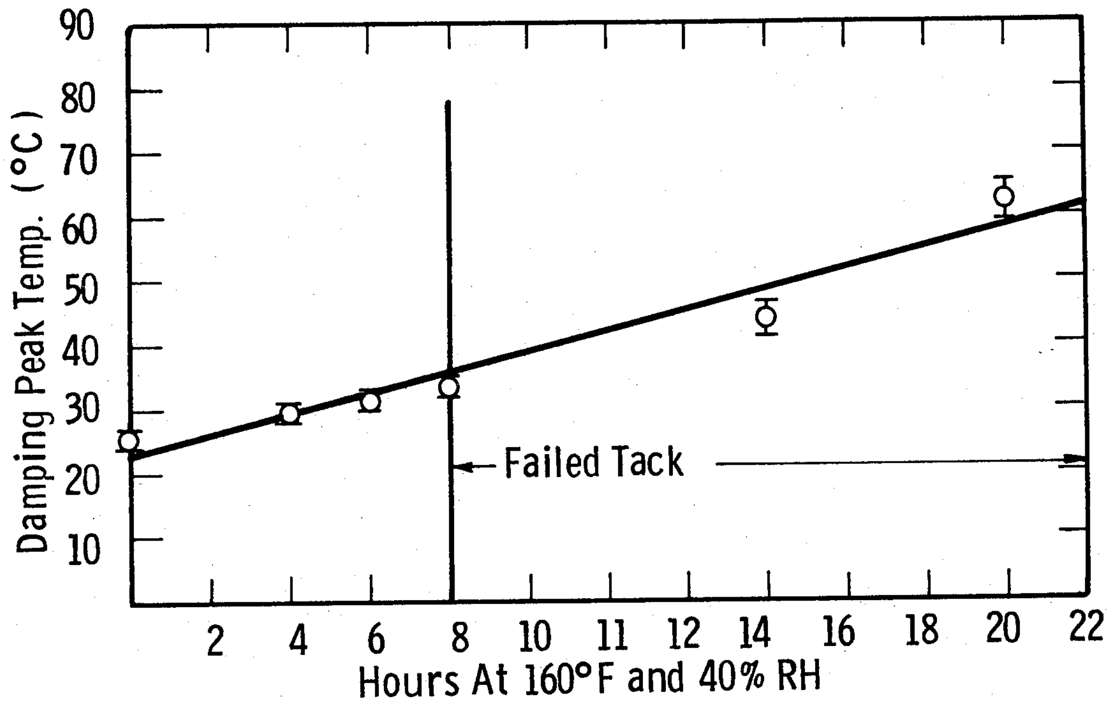


Fig. 15 – Aging at 160°F and 40% RH, MF batch, DMA data

Curve 716691-A

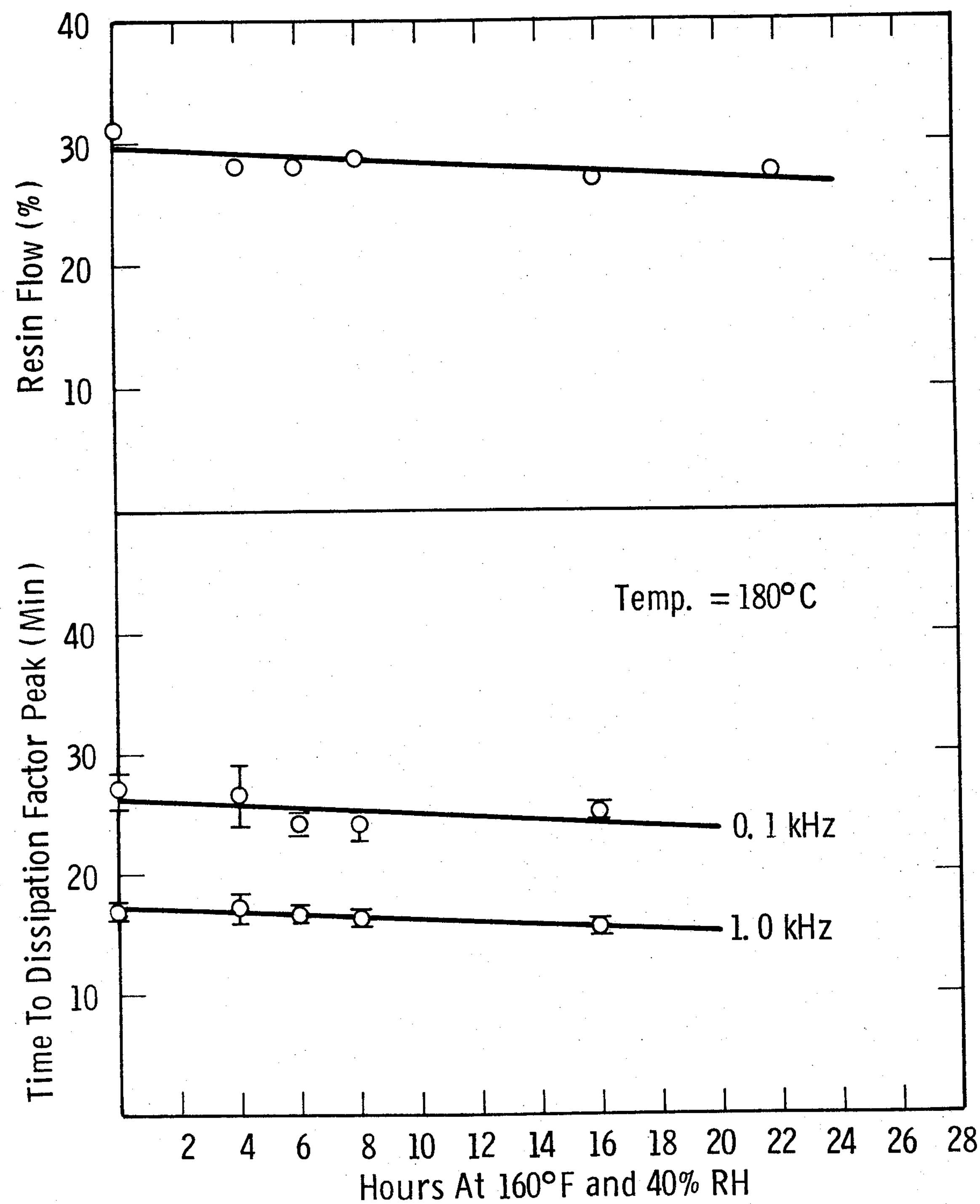


Fig. 16 — Aging at 160°F and 40% RH, MF batch
Dielectric analysis and resin flow data

Curve 717865-A

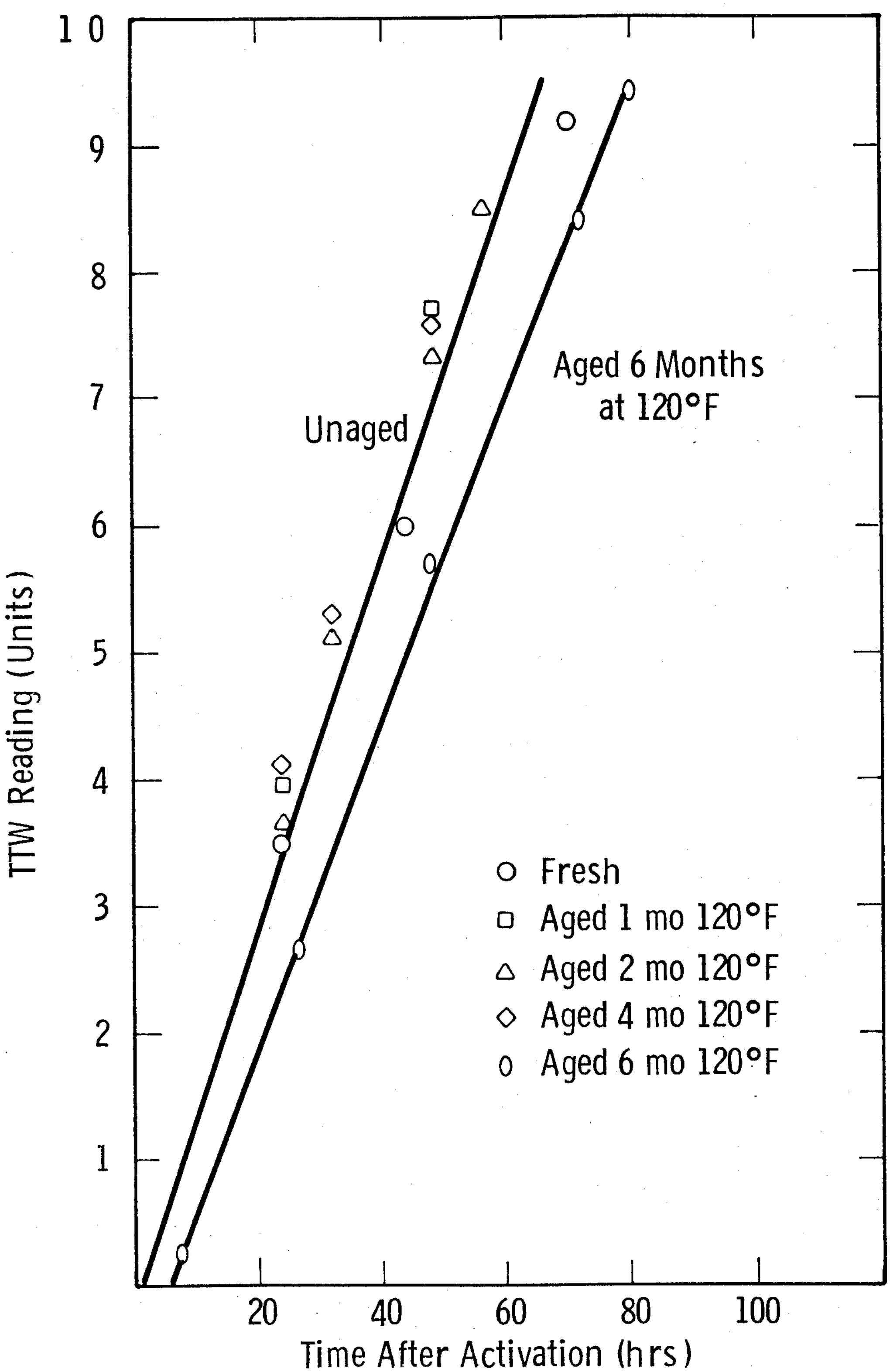


Fig. 17 — Long term aging of TTW T33 at 120°F then activated and recorded at 120°F

## 4.8 AGING OF MONITORMARKS

The special long-term Monitormarks obtained from 3M Co. were activated and aged along with 3501-6/AS prepreg at several temperature-humidity conditions of interest to this program (viz., 74°F and 20% RH, 74°F and 80% RH, 120°F and 160°F and 40% RH). Figure 18 shows the data for Monitormark 15Q. The lines represent an average of at least three samples for the indicated conditions. Monitormarks 5R and T7 had nearly identical readings under these aging conditions and are therefore averaged together and the data are shown in Figure 19 - each line being the average of three 5R samples and three T7 samples.

Figures 18 and 19 also show for each aging condition, the point in time when the prepreg loses its tack, i.e., the end of its useful life. This point is indicated on each curve by a black dot and this shows why the Monitormarks in their present design cannot serve as overage indicators for 3501-6/AS prepreg. Depending on the aging condition chosen, end of the useful life of the prepreg can occur when the readings are anywhere from 0.2 to 5.0, as shown in Figures 18 and 19. This constitutes the whole range of the device and therefore a reading cannot be selected which would serve to indicate a possible overage condition. Monitormarks were also aged at 104°F and 104°F, 90% RH and the readings fall in the same narrow band of readings shown in Figures 18 and 19. Loss of tack at 104°F occurs at about four days.

One advantage the Monitormark has over the TTW is that it is relatively unaffected by high humidity. It is also possible for the manufacturer to design a product such that it may be useful in this application.

## 4.9 SUMMARY OF AGING STUDIES WITH 3501-6/AS PREPREG

The aging studies have shown that under different aging conditions, several methods can be found that can reliably track the age of the prepreg and can give a test value (called here the critical value) which can be used to determine when the useful life of the prepreg is over. In our

Curve 716031-A

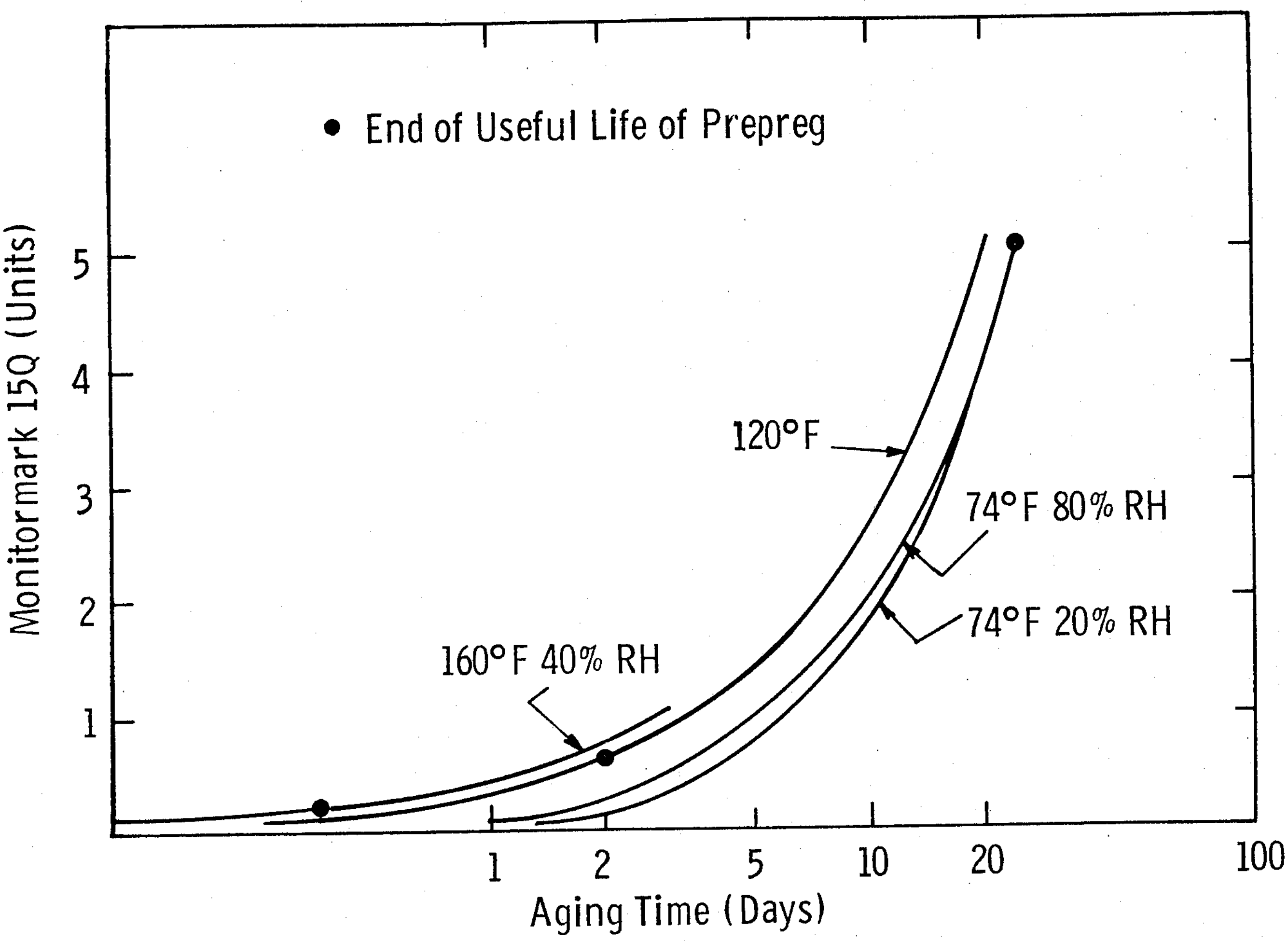


Fig. 18– Aging behavior of Monitormark 15Q under various temperature and humidity conditions

Curve 716032-A

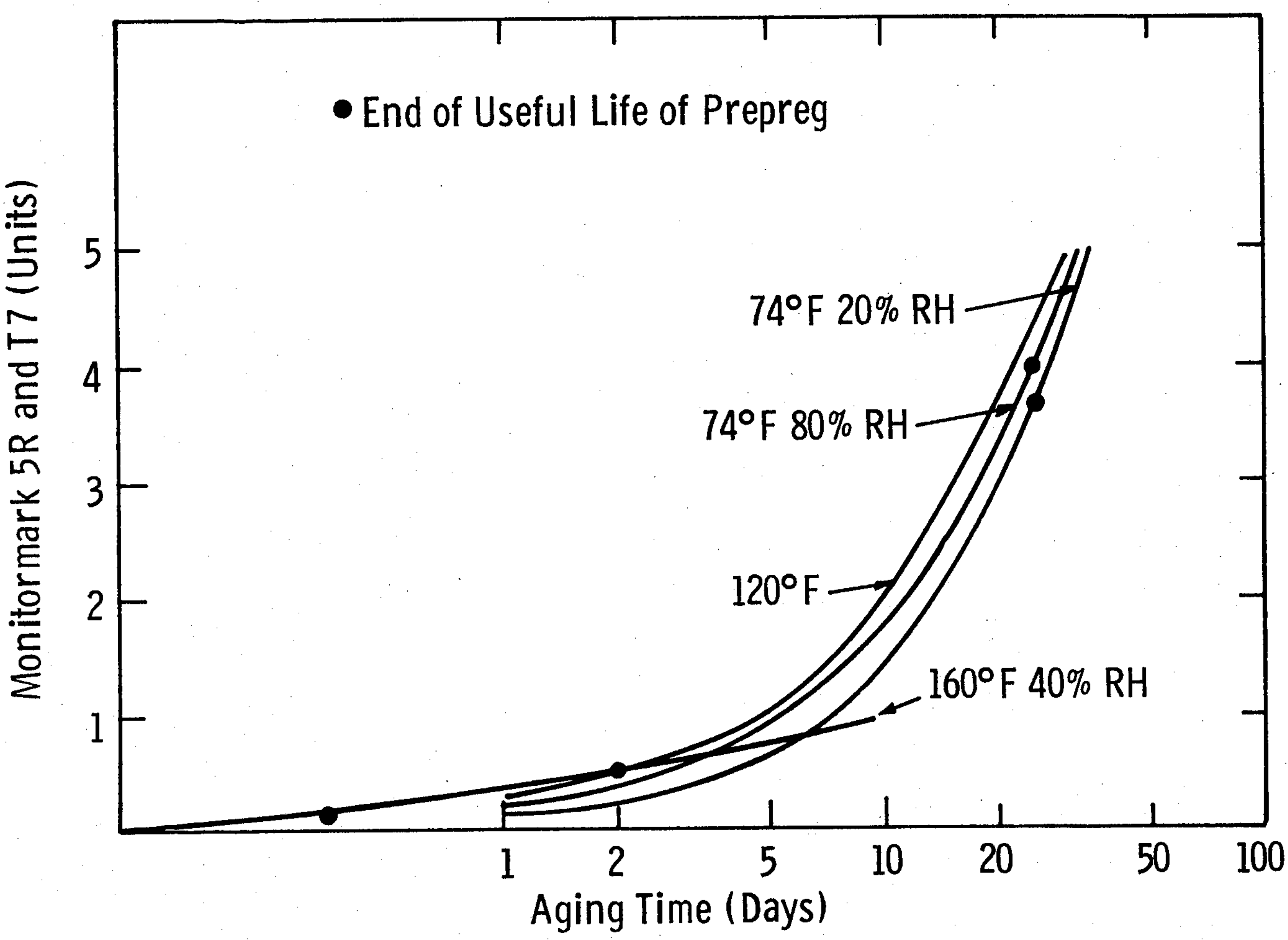


Fig. 19– Aging behavior of Monitormarks 5R and T7 under various temperature and humidity conditions

studies, the value of the age indicating test was correlated to the loss of prepreg tack. It is also possible to obtain a value which would correlate with the loss of some other property if that property is considered more critical.

The age indicating methods, the critical value obtained with the 3501-6/AS prepreg, and the relative merits are discussed below:

- Time-Temperature Watch: This type of time temperature integrator was found to be quite accurate. Within limited ranges of temperature, it was able to indicate when the prepreg would lose its tack. Figure 20 shows a summary of the aging data for the TTW Type 33. All eight conditions at which the aging behavior of 3501-6/AS and the Type 33 was examined are shown. At each aging condition the end of the useful life of the prepreg (loss of tack) was determined (see Section 4.1) and is marked on Figure 20 with a black dot. The reading at that point is the critical value for the indicator. An ideal indicator would have only one critical value. The Type 33 TTW has critical values ranging from 4 (under high humidity conditions) to 6.5. A conservative number to use would be a reading of 4 units. The chief merit of the TTW lies in its simplicity of use and low cost. It is ideally suited for use where other more technically elaborate methods cannot be used. It has to be carried with the prepreg at all times. While its readings are slowed down by high humidity exposure, the change appears not critical for this application. Where critical, the packaging can be improved to overcome or reduce this effect.

- Dielectric Analysis: This method can accurately follow the aging of the prepreg and correlate a critical value of a property with the loss of tack. The property is the temperature of the peak in dissipation factor at 1 kHz. Using our sample configuration and heat-up rate, this was found to be 62°C ± 2°C. Isothermal methods were not as successful, and the only problem encountered was the effect of humidity which can be overcome by drying the samples prior to test.

Curve 716030-A

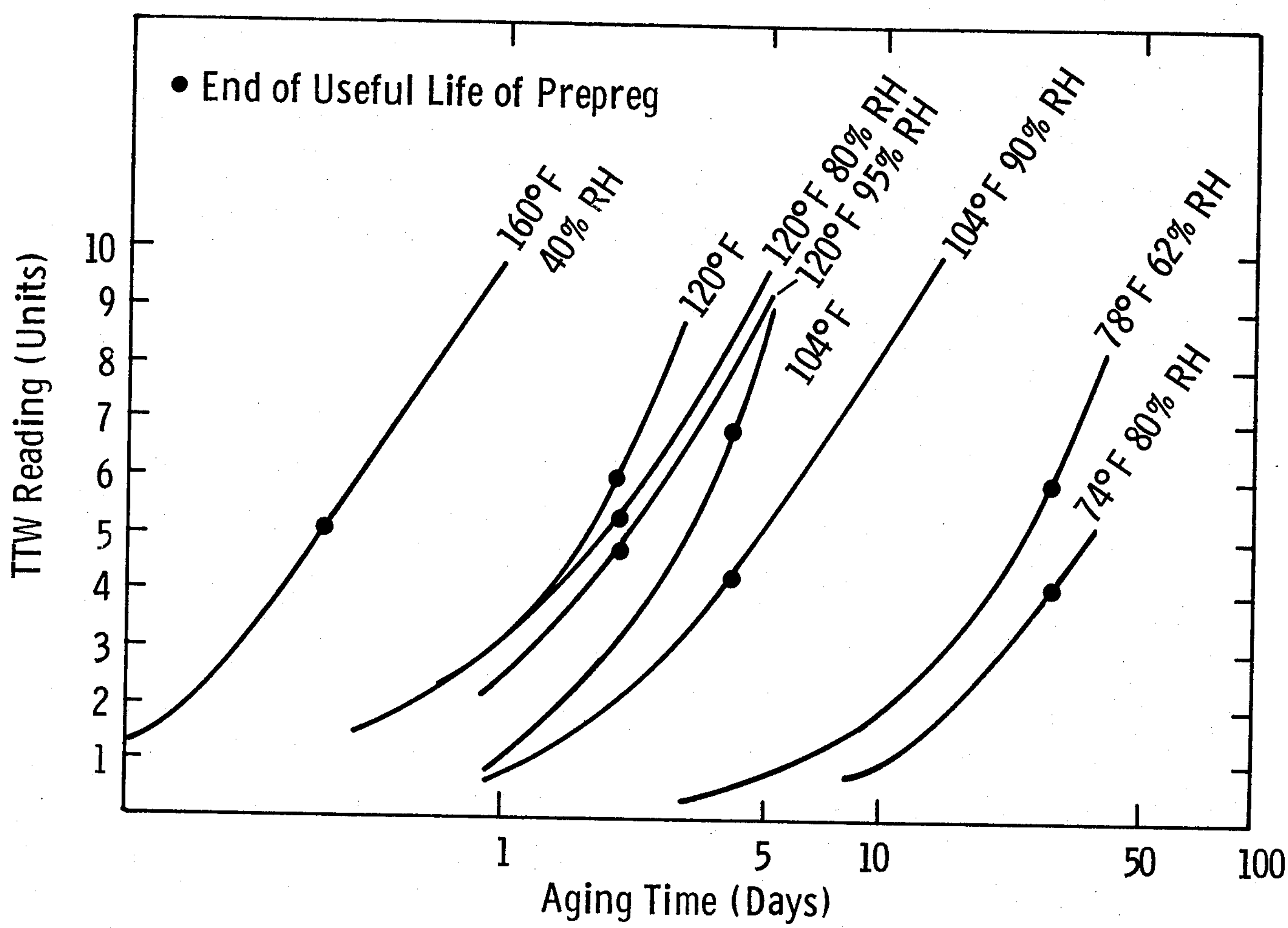


Fig. 20— Aging behavior of TTW Type 33 under various temperature and humidity conditions

Figure 21 is a summary of the dielectric analysis (DA) data using the temperature variant mode of operation. For seven aging conditions it shows the temperature of the 1 kHz peak in dissipation factor measured as the 3501-6/AS prepreg ages. On each aging curve, a black dot indicates the time at which the prepreg reached the end of its useful life, as denoted by loss of tack. The temperature reading of the peak corresponding to that time becomes the critical value for the use of DA as an overage indicator. This critical value is 62 ± 2°C.

· Dynamic Mechanical Analysis (DuPont 980 DMA): This method is quite accurate and sensitive provided the experimental conditions (including thermocouple location) are kept absolutely identical each time. The property that correlates well with prepreg age is the temperature of the relative damping peak. Figure 22 shows a summary of all the aging studies in which DMA was used to follow prepreg age. As the prepreg ages under different conditions, the relative damping peak temperature increases. As in Figures 20 and 21, the black dot marks the point in time when the prepreg reached an overage condition. Except for one aging condition, the critical value for the temperature of the relative damping peak is 32 ± 3°C.

## 5. EFFECT OF MOISTURE ON THE RELATIVE REACTION RATE OF 3501-6/AS PREPREG

This section of the report describes the results of the study carried out to determine the effect of moisture on the curing rate of 3501-6/AS prepreg. It is a preliminary attempt to clarify the effect of moisture on the chemistry of the prepreg resin under aging conditions during which the prepreg is exposed to high humidity. The consequences to laminate properties were not investigated due to schedular constraints. This information should be of particular interest to those using the prepreg (or other materials of similar chemistry) for repairs or where a controlled environment cannot be obtained.

Curve 716029-B

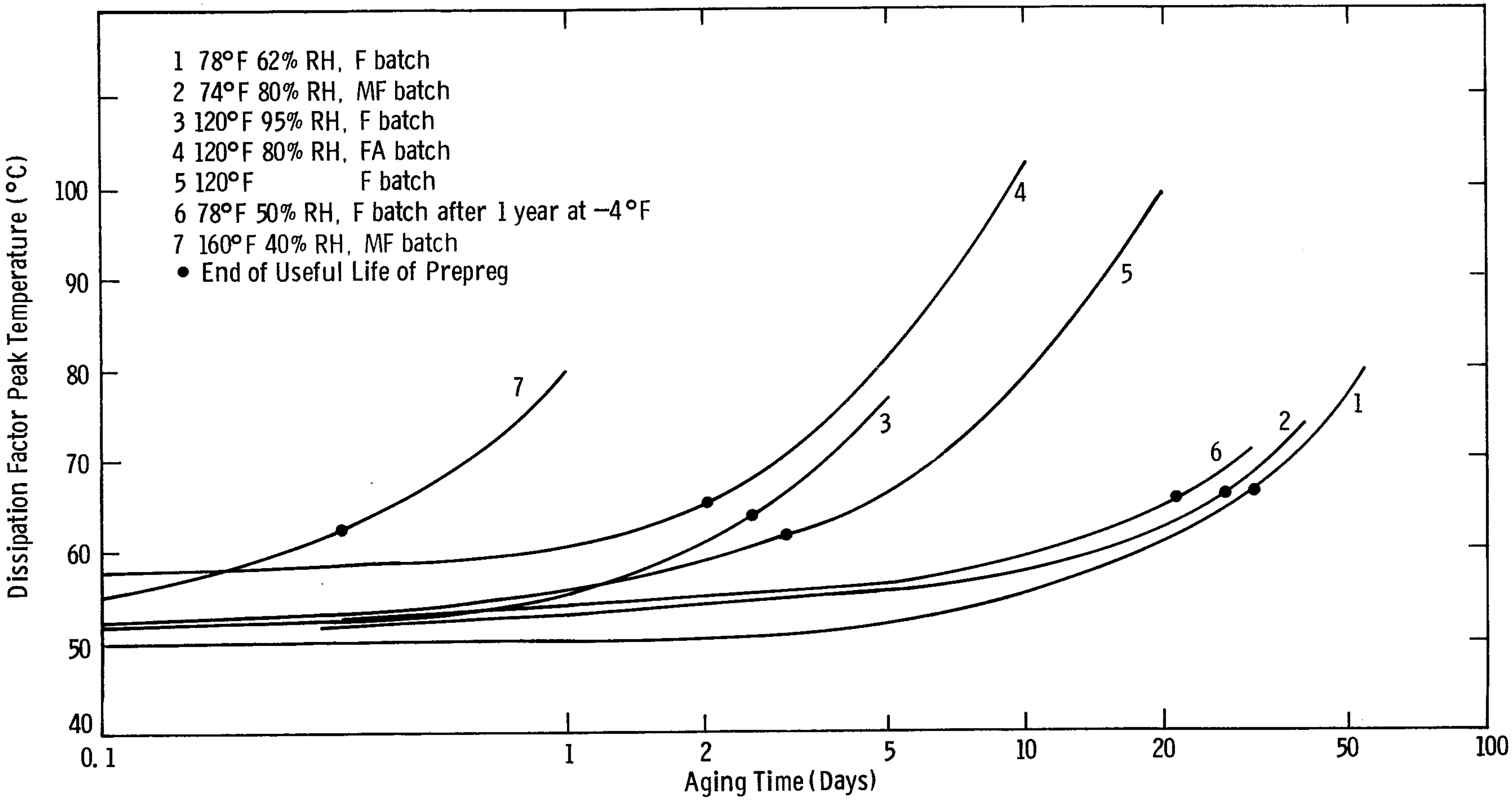


Fig. 21— Dissipation factor peak temperature as a function of aging time under various aging conditions for 3501-6/AS prepreg. ● Symbol indicates loss of prepreg tack and occurs when peak temperature is between 62 and 66°C

Curve 718224-A

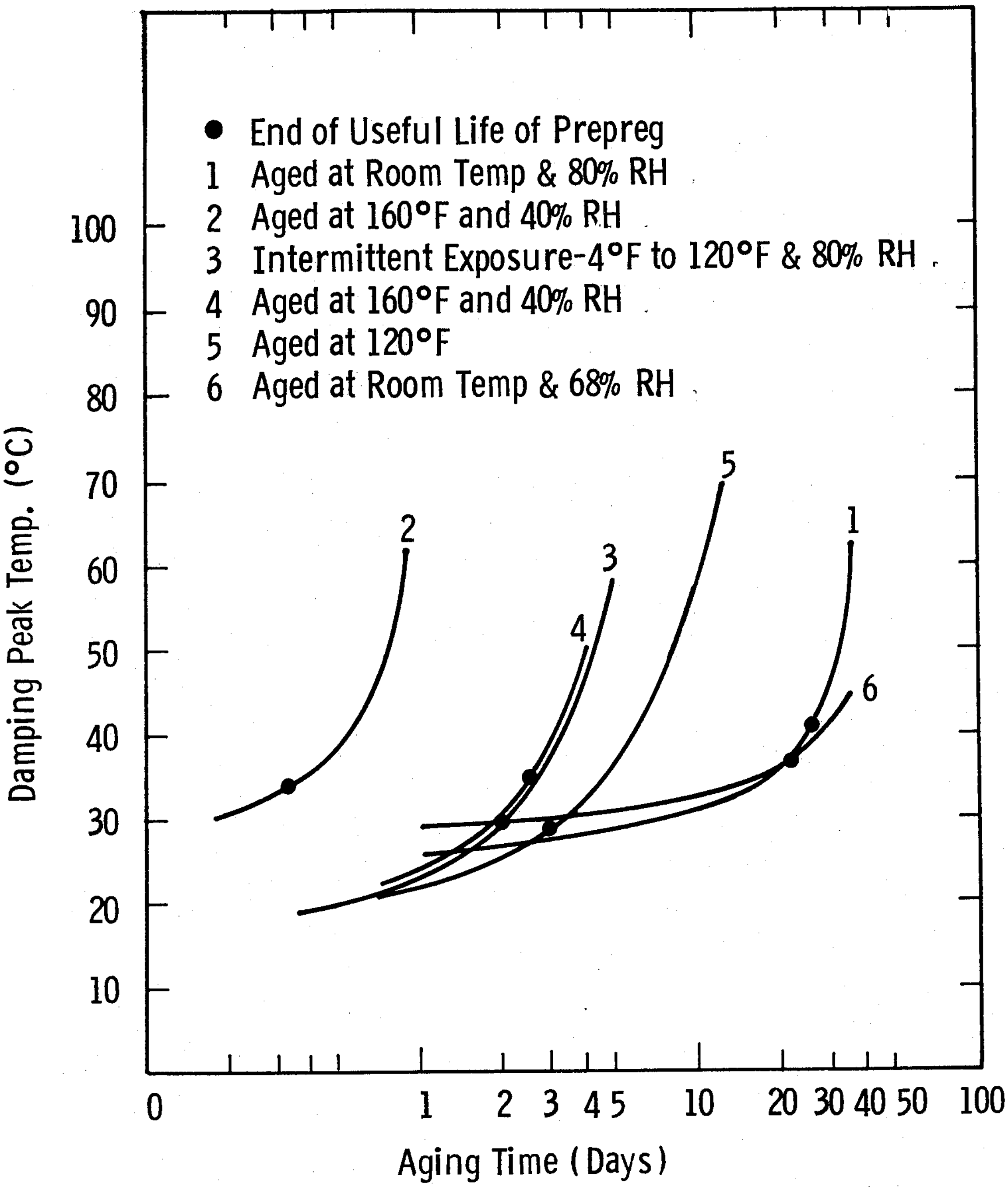


Fig. 22 – DMA data. Damping peak temperature as a function of aging time under various aging conditions for 3501-6/AS prepreg. ● Symbol indicates loss of prepreg tack

Three temperature and humidity conditions were examined and the results are described below. Experimental techniques were described in Section 3.2 and therefore a discussion of methods is not included here.

## 5.1 120°F, 80% RH AGING

Unaged samples of 3501-6/AS prepreg were found to contain 0.22% moisture. The amount of moisture picked up by the prepreg aged at 120°F, 80% RH reached a nearly constant value of 0.4% in less than two days, as shown in Figure 23 (lower). Thereafter, the change was gradual.

Figure 23 (middle) also shows that resin flow of the prepreg decreased as a function of aging time. While the differences were rather small, samples aged at 120°F, 80% RH showed a steadier, more rapid decrease in resin flow than those aged in control conditions.

Figures 24, 25 and 26 show the Arrhenius plots for the prepreg reaction at two, four and six days aging at 120°F under 80% RH and the control conditions. The base line is also given for unaged prepreg. The samples aged under control conditions show longer times to tan $\delta$ peaks, indicating slower relative reaction rates. Although samples aged two days under 80% RH also showed this decreased relative reaction rate at temperatures greater than 170°C, those aged under humidity for four and six days exhibited a greatly increased reaction rate at temperatures less than 180°C. Figure 27, a composite for the humid aged samples, shows that as the aging period increased, the relative reaction rate of the prepreg increased (as indicated by decreased time to tan $\delta$ peaks). This is especially apparent with analysis temperatures less than 190°C.

The activation energy (slope of the Arrhenius line) of the control samples remained nearly the same as that of the base line (unaged) samples, an indication that no change in reaction mechanism had taken place during aging under control conditions. Prepreg aged at 80% RH, on the other hand, showed a significant change in activation energy. The activation energy of these humidity aged samples is shown in Figure 23 (top) as a function of aging period. After aging only four days, the activation

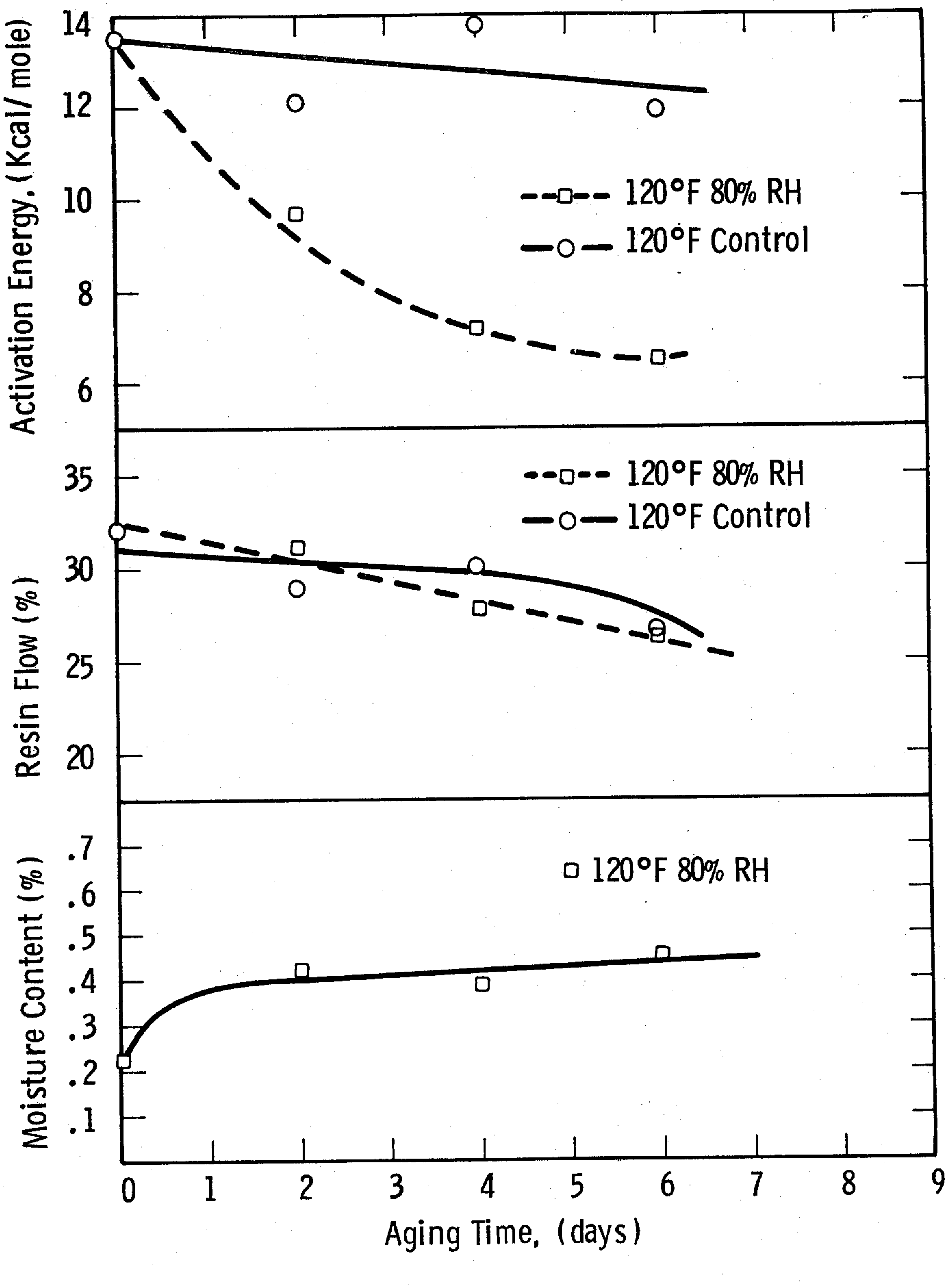


Fig. 23– Activation energy, resin flow, and moisture content of the 3501-6/AS prepreg after aging at 120°F

Curve 717866-A

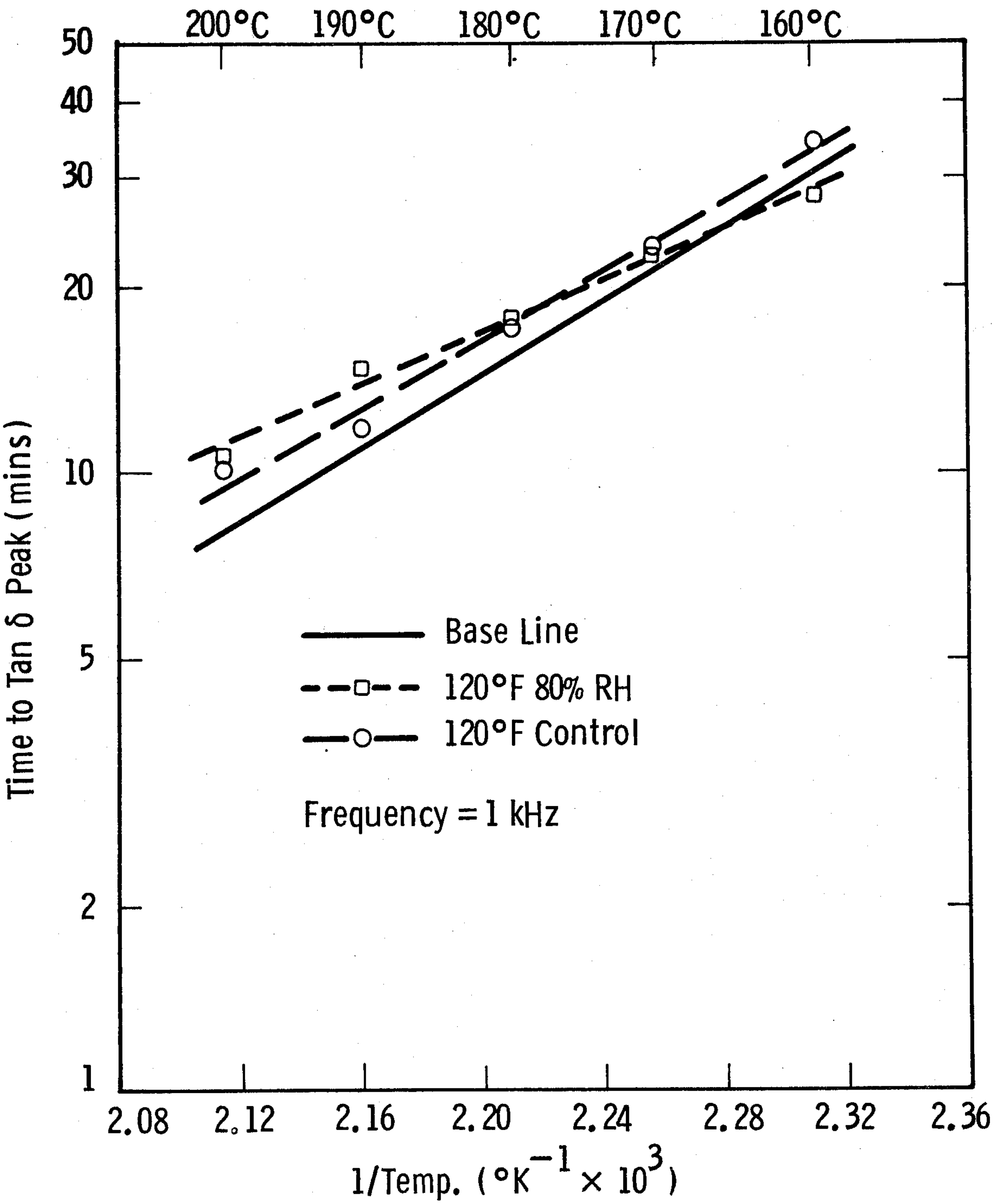


Fig. 24– Arrhenius plot for the reaction of the prepreg after 2 days aging at 120°F

Curve 717857-A

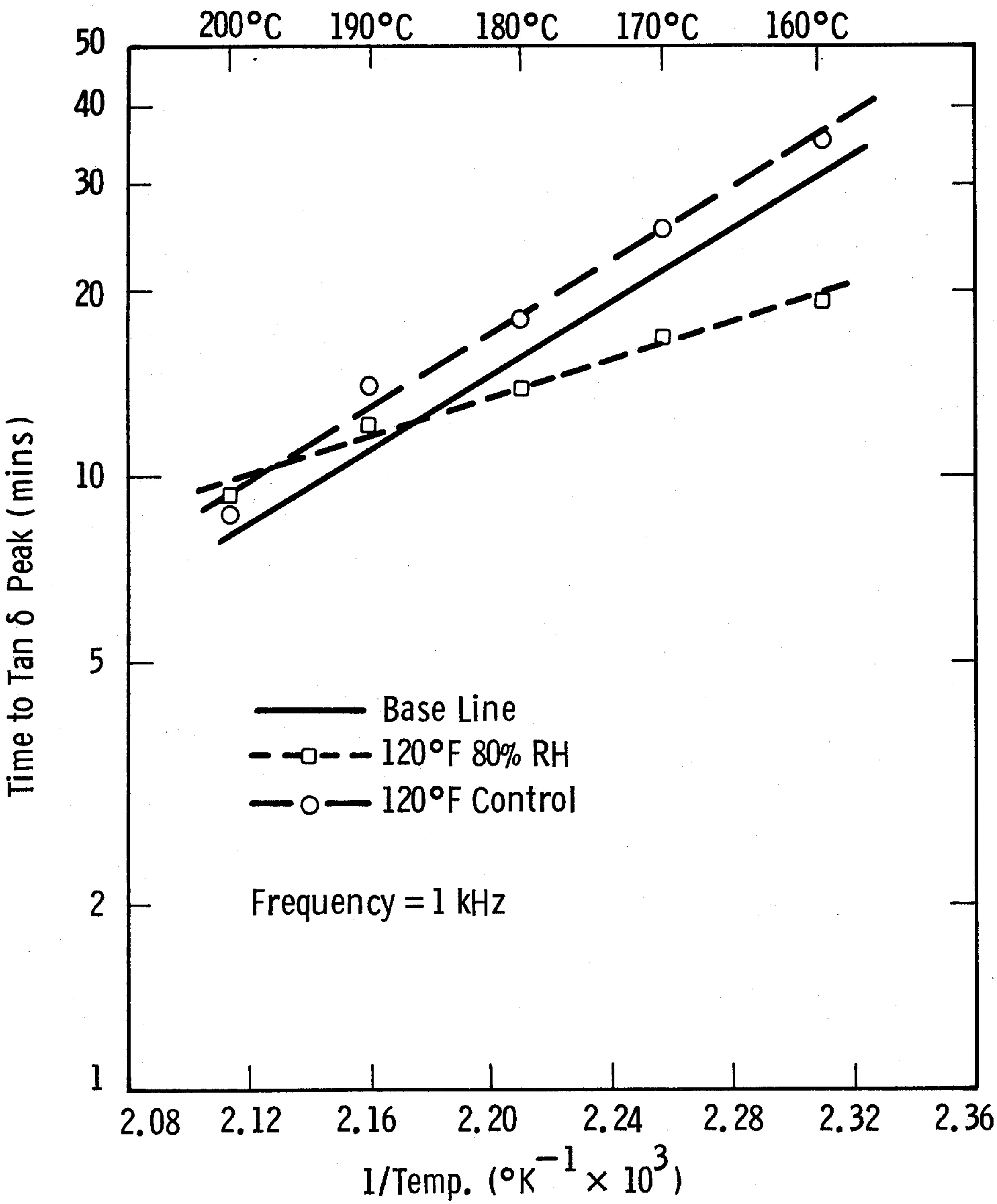


Fig. 25 — Arrhenius plot for the reaction of the prepreg after aging 4 days at 120°F

Curve 717858-A

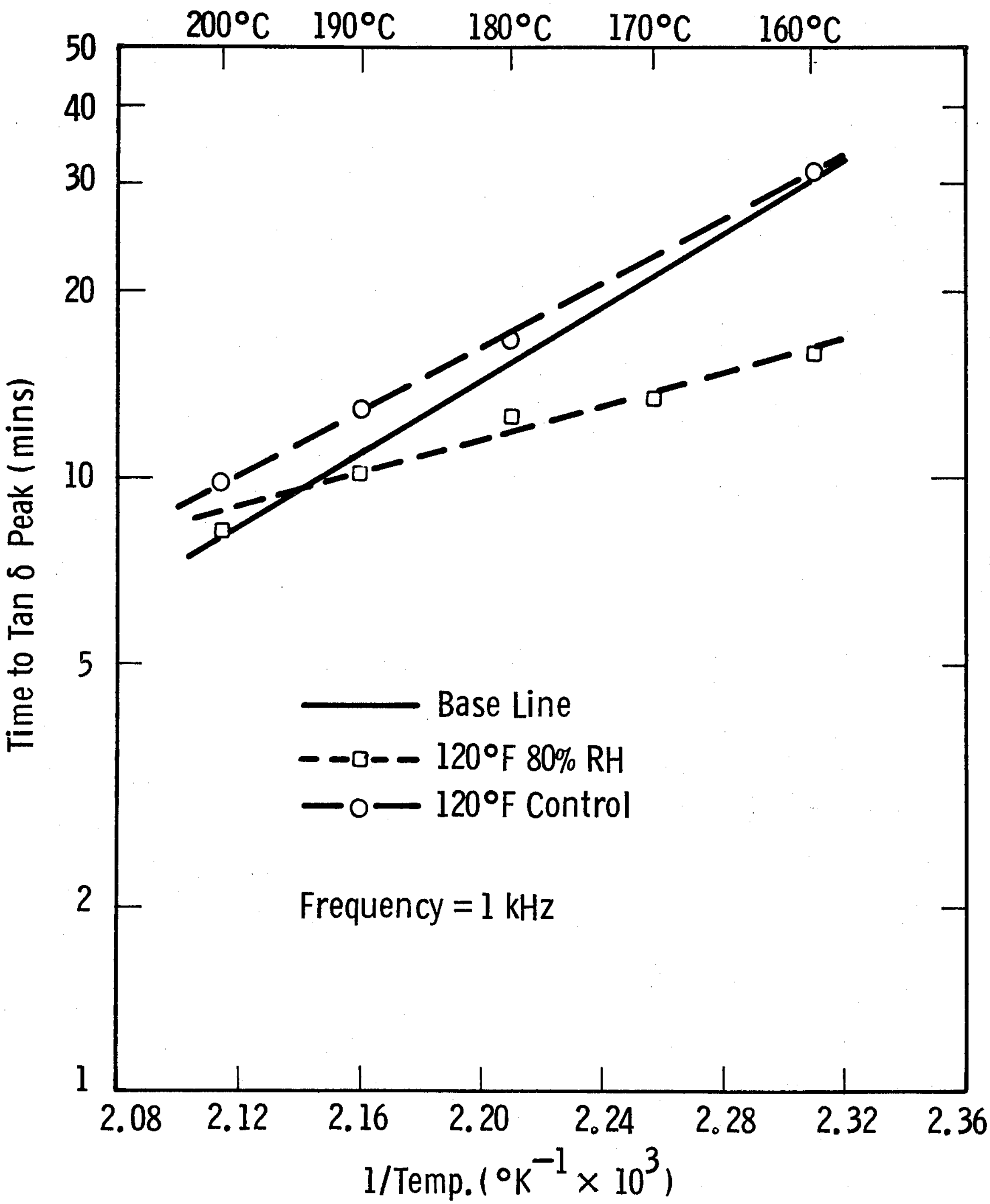


Fig. 26 — Arrhenius plot for the reaction of the prepreg after aging 6 days at 120°F

Curve 717859-A

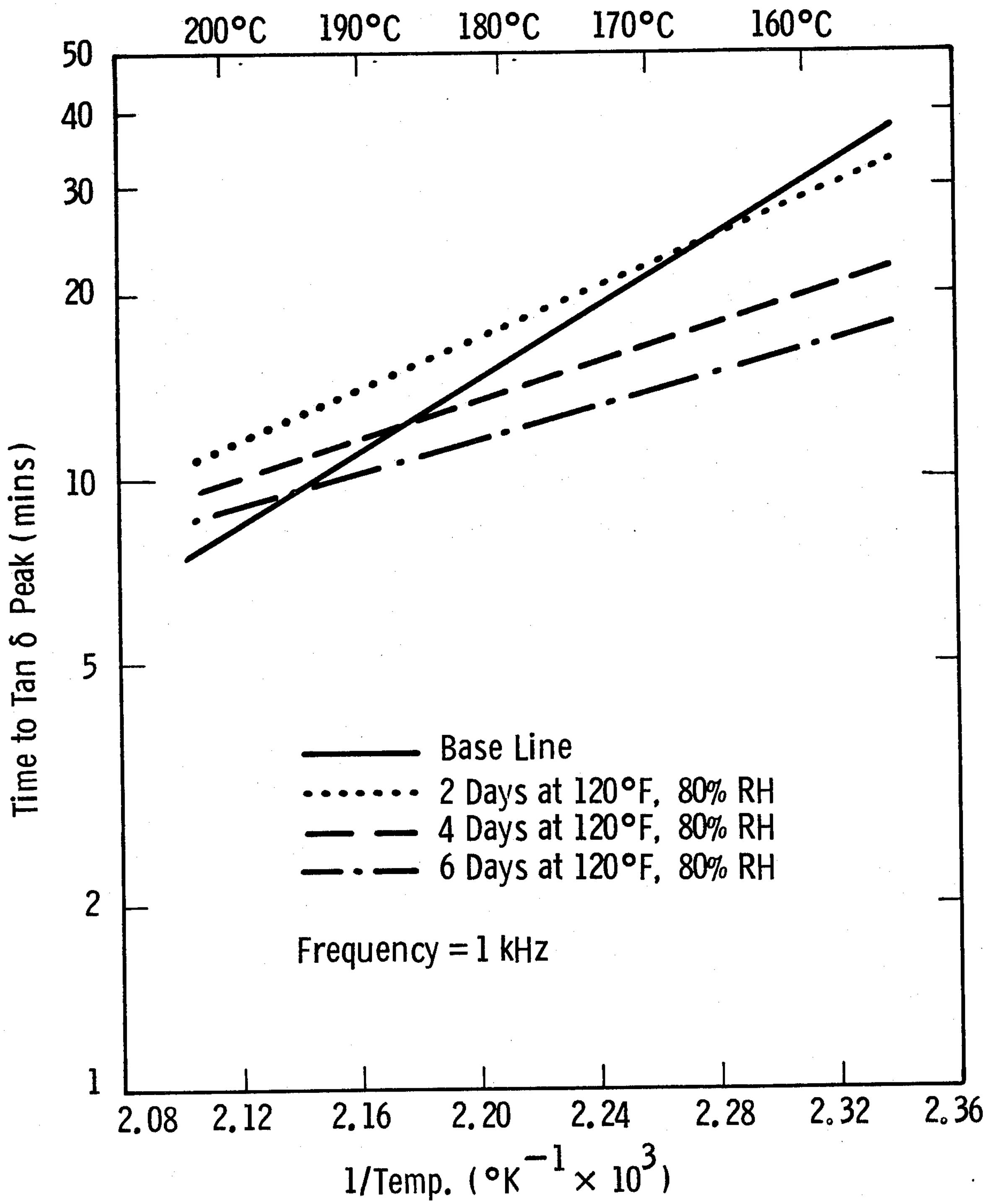


Fig. 27 — Arrhenius plot for the reaction of the prepreg aged at 120°F and 80% RH

energy had decreased to nearly one-half that of unaged prepreg. This indicates that a change in the reaction mechanism of the prepreg had taken place during the aging period. The humidity aged samples were all desiccated to about their original moisture content prior to dielectric analysis to insure that the observed changes in reactivity were not due to erroneous dielectric effects of the "free" water in the prepreg. ("Wet" samples, not desiccated prior to dielectric analysis, were also tested and were found to give results almost identical to the desiccated samples.) Since the only difference in the aging environment between the control and experimental samples was the humidity conditions, the changes in reactivity may only be attributed to moisture absorbed by the prepreg during aging.

Also, the fact that the excess moisture absorbed by the prepreg during aging was removed prior to analysis shows that the changes are irreversible. That is, removal of the excess water did not restore the original reactivity of the prepreg.

### 5.1.1 Liquid Chromatography (LC)

LC was used on prepreg aged at 120°F, 80% RH and 120°F control to determine the changes in the chemical components as described in Section 3.2. The peak heights of the eluting components (TGMDA, DDS and reaction product) were measured. Since the detector was a variable wavelength UV spectrometer, an absolute response was calculated in terms of absorbance units per mg at 280 nm. This absolute response would be proportional to the amount of the component present in the soluble state. The results, shown in Table 2, indicate that the amount of each monomer is reduced with aging at 120°F and that the sample aged at 80% RH was comparatively much more reacted than the sampled age for a similar period of time at 120°F control condition. The data also show that there is less total extractable present (i.e., there is more polymer formed) in the humid aged samples than in the control samples.

To correct for this, the solutions were filtered and an aliquot portion was taken to dryness to determine the total amount of soluble material present. These results are shown in Table 3.

TABLE 2

LC DATA FOR 3501-6/AS PREPREG AGED AT 120°F
(UNCORRECTED FOR SOLUBILITY)

| | Absorbance Units/mg of Sample | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 Days | 2 Days | | 4 Days | | 6 Days | |
| | | Control | 80% RH | Control | 80% RH | Control | 80% RH |
| TGMDA | 1.82 | 1.05 | 0.87 | 1.01 | 0.84 | 0.92 | 0.55 |
| DDS | 2.60 | 1.77 | 1.35 | 0.99 | 0.55 | 0.94 | 0.20 |
| Reaction Prod. | -- | 0.25 | 0.37 | 0.18 | 0.15 | 0.24 | 0.09 |

TABLE 3

FRACTION OF 3501-6/AS PREPREG THAT IS SOLUBLE AFTER
AGING AT 120°F (RESIN CONTENT OF PREPREG = 43%)

| | % Soluble | |
|---|---|---|
| Aging Time | 120°F Control | 120°F 80% RH |
| 0 | 43.0 | 43.0 |
| 2 | 42.8 | 41.2 |
| 4 | 45.5 | 39.8 |
| 6 | 43.2 | 28.7 |

This indicates that the control samples show approximately the same amount of soluble material through the aging period while the sample aged at 80% RH shows a rapid decrease in the amount of soluble material. When the response data from the UV detector (Table 2) is corrected for the soluble organic portion (Table 3) the corrected data shown in Table 4 are obtained.

Table 4 shows that for each time period, the samples aged at 80% RH contained less monomer than the corresponding control sample. This indicates that in the presence of moisture, the reactivity of the resin mix of this prepreg is enhanced.

TABLE 4

LC DATA FOR 3501-6/AS PREPREG AGED AT 120°F (SOLUBLE FRACTION)

| | Absorbance Units/mg of Soluble Fraction | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 Days | 2 Days | | 4 Days | | 6 Days | |
| | | Control | 80% RH | Control | 80% RH | Control | 80% RH |
| TGMDA | 4.24 | 2.47 | 2.12 | 2.23 | 2.12 | 2.13 | 1.92 |
| DDS | 6.07 | 4.13 | 3.28 | 2.18 | 1.38 | 2.17 | 0.69 |
| Reaction Prod. | -- | 0.59 | 0.89 | 0.39 | 0.38 | 0.56 | 0.31 |

## 5.2 100°F, 80% RH AGING

Figure 28 shows the changes in moisture content and resin flow as a function of aging time for the 3501-6/AS prepreg. The prepreg reached a nearly constant moisture content of about 0.38% after only two days. Resin flow data was quite scattered and no significant difference was seen between control and 80% RH samples.

Figures 29-31 show Arrhenius plots for both control and humidity aged samples. After three days aging, no change in activation energy (slope of the Arrhenius line) of the prepreg was observed. However, a significant decrease in the relative reaction rate of the 80% RH samples occurred, while that of the control samples remained almost identical to the base line. As the aging time increased, the reaction rate of the control decreased while the activation energy remained relatively unchanged. The humidity aged samples, on the other hand, showed increasing relative reaction rates at lower analysis temperatures, accompanied by decreasing activation energies. Figure 28 shows the change in activation energy as a function of aging period. After nine days aging at 100°F, 80% RH, it was 10.6 Kcal/mole as compared to 13.5 Kcal/mole for unaged prepreg. Although the changes in activation energy were significant, they were not as drastic as those encountered at 120°F, 80% RH aging.

Curve 717860-A

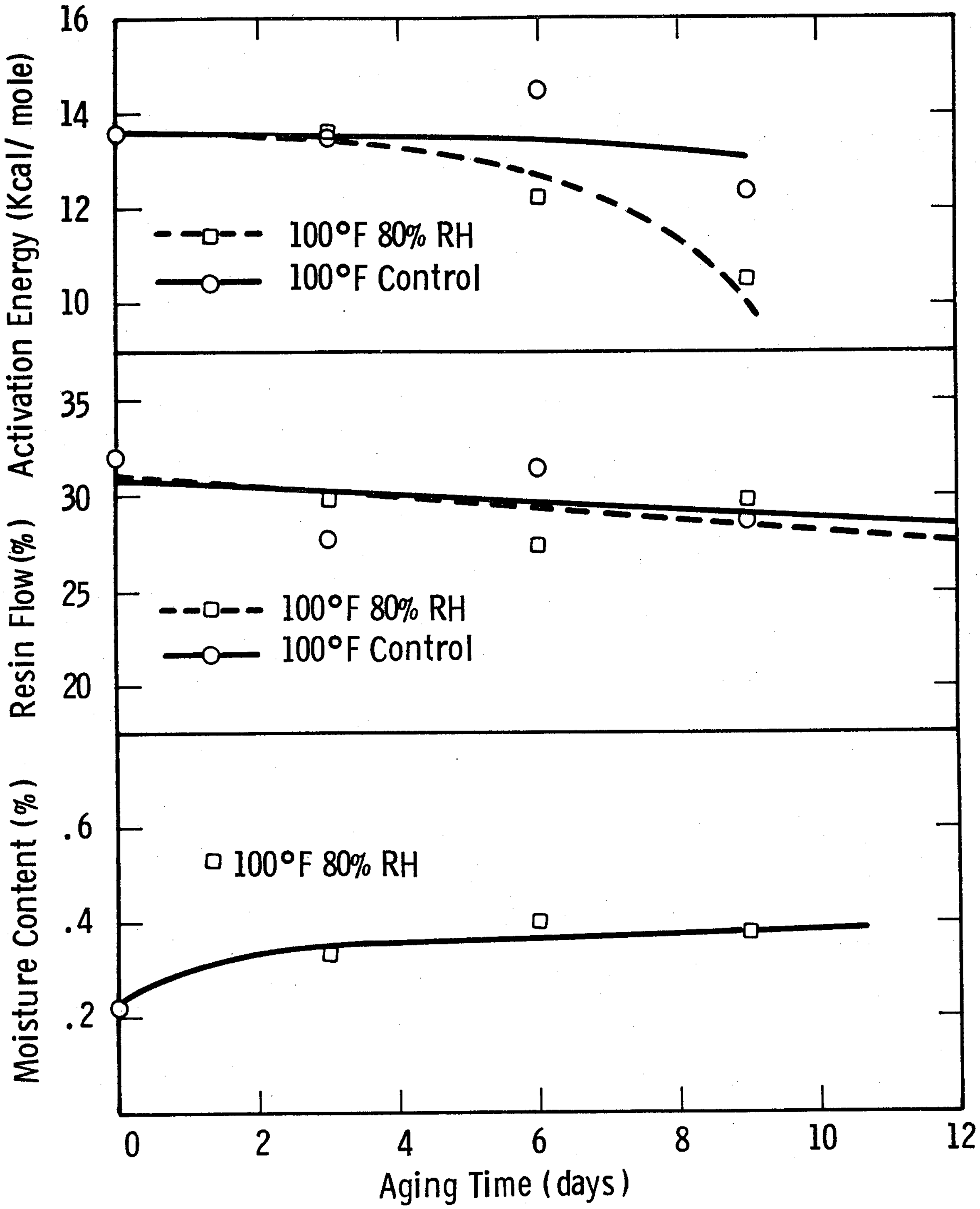


Fig. 28— Activation energy, resin flow, and moisture content for 3501-6/AS prepreg aged at 100°F

Curve 717861-A

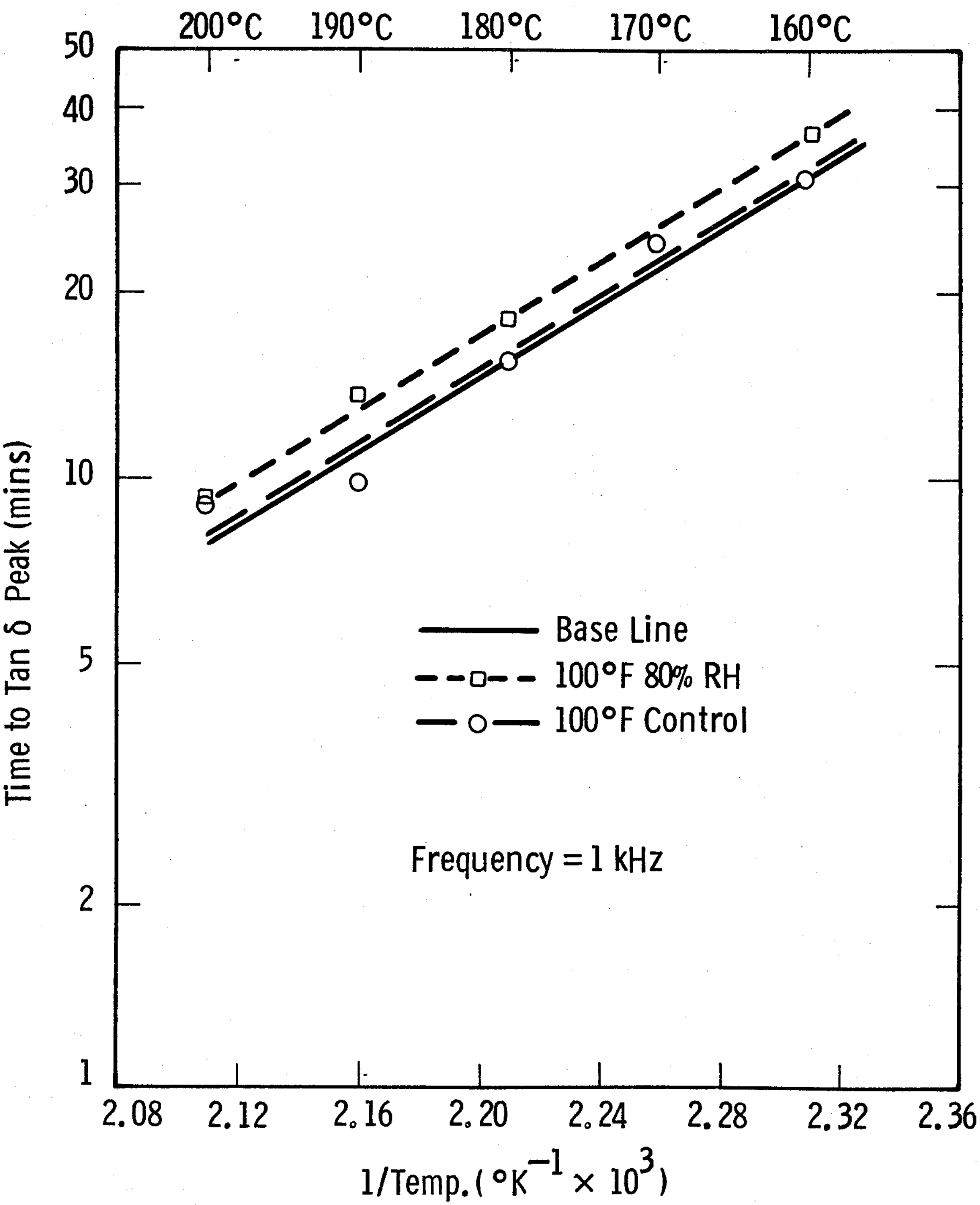


Fig. 29— Arrhenius plot for the reaction of the prepreg after aging 3 days at 100°F

Curve 717862-A

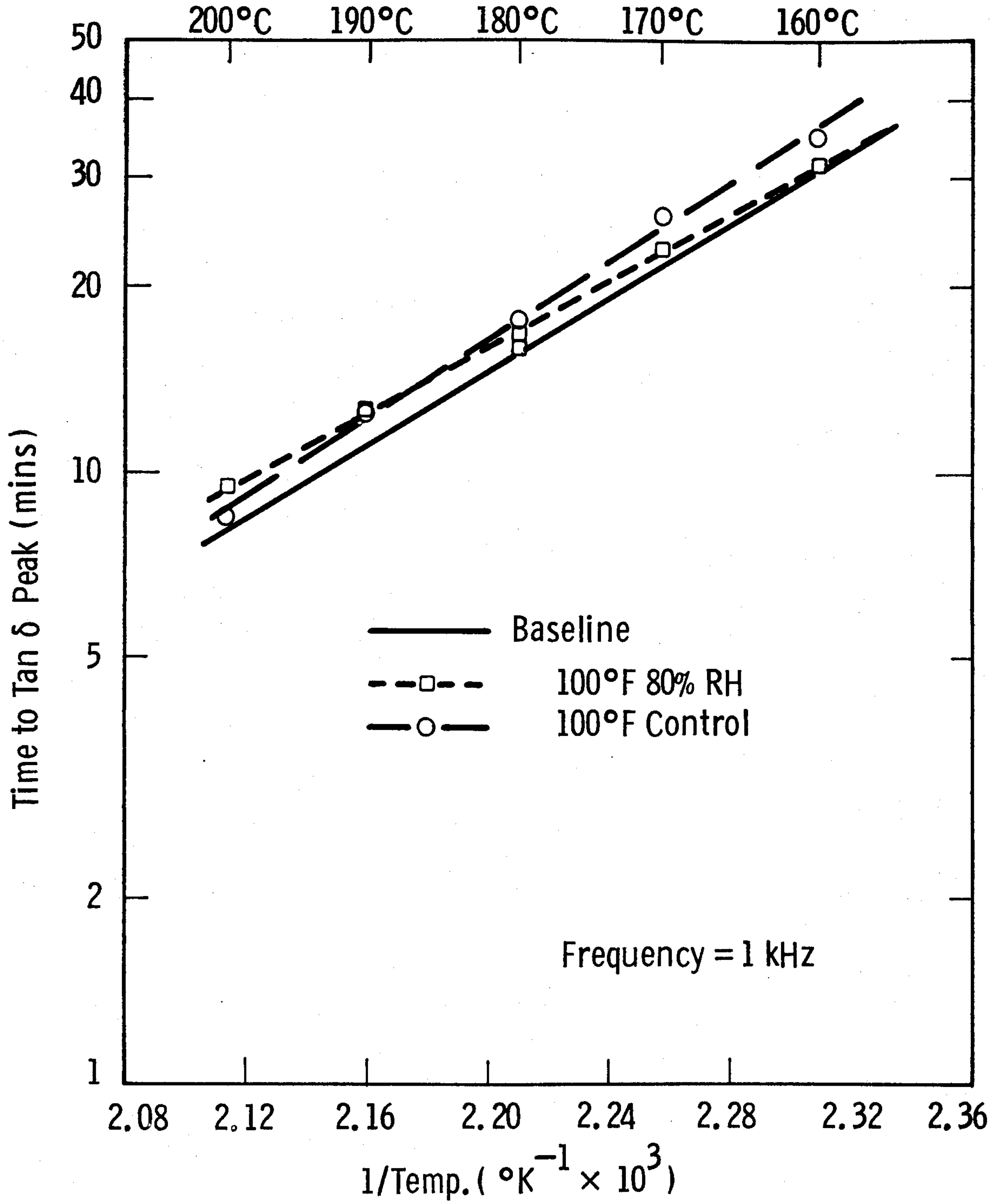


Fig. 30 – Arrhenius plot for the reaction of the prepreg after aging 6 days at 100°F

Curve 717863-A

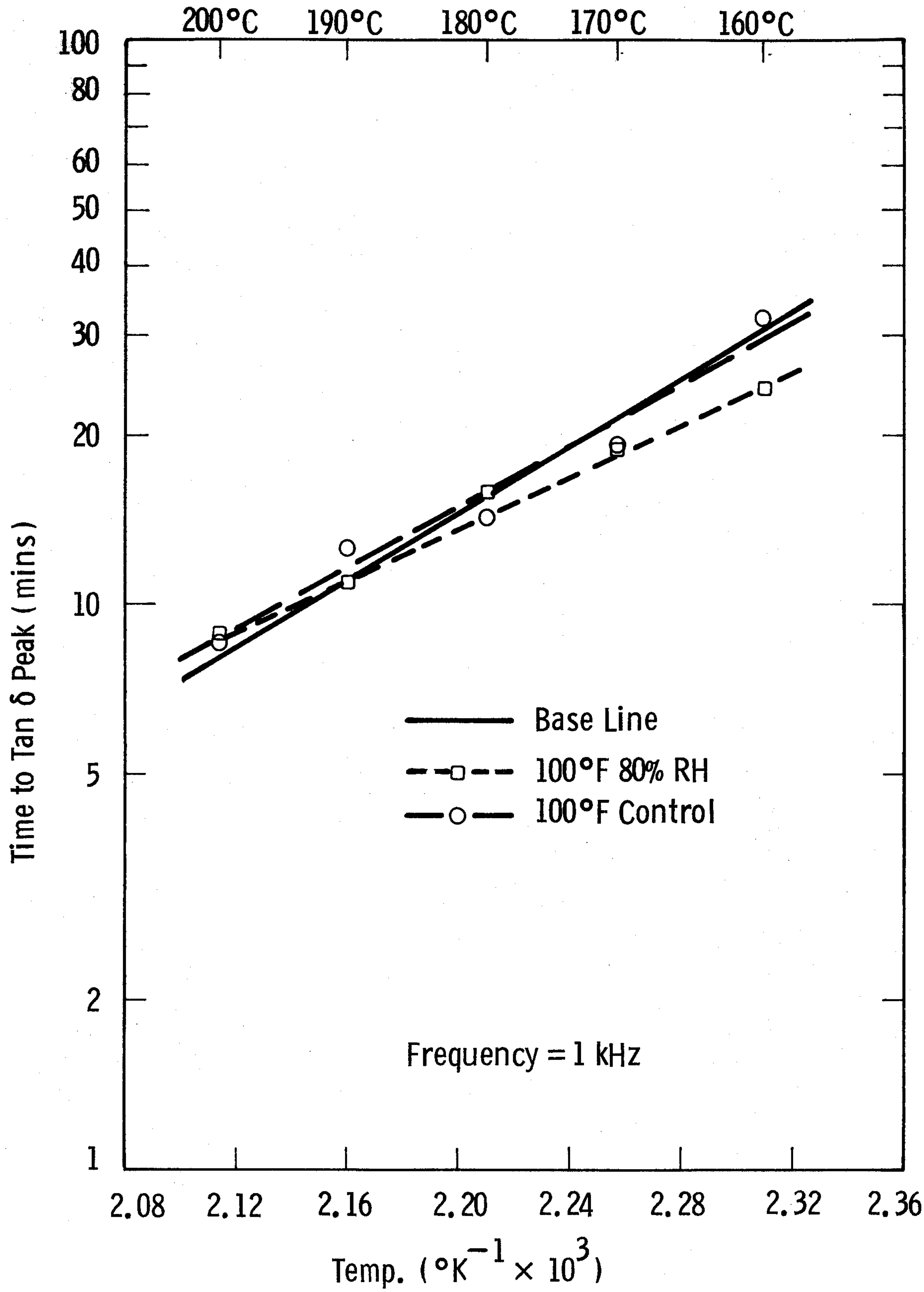


Fig. 31 – Arrhenius plot for the reaction of the prepreg after aging 9 days at 100°F

## 5.3 ROOM TEMPERATURE, 90% RH AGING

Figure 32 shows the moisture content and resin flow data for prepreg aged at room temperature. Moisture content values leveled off at about 0.7% after six days aging at 90% RH. Resin flow decrease was slow for the first 15 days, but, for humid aged samples, decreased rapidly between 15 and 21 days.

Arrhenius plots for the prepreg aged at room temperature were obtained after aging periods of 3, 6, 9, 13, 16 and 21 days. For simplicity, only the plots for 6, 13 and 21 days have been shown (Figures 33-35, respectively). The changes in the reactivity of the prepreg at ambient temperature were much slower than at the other aging conditions. Figure 34 shows 13 days aging which resulted in slower relative reaction rates for both control and humidity aged samples, with no major change in activation energy. Figure 35 shows that after 21 days aging the relative reaction rate for the control samples had not changed much from the initial (base line) reaction rates. The humidity aged samples, however, showed an increased reaction rate accompanied by a decreased activation energy of 11.25 Kcal/mole as compared to 13.5 Kcal/mole for unaged prepreg. Figure 32 shows that the decrease in activation energy for prepreg aged at room temperature was not very significant until at least 16 days aging.

## 5.4 DISCUSSION OF MOISTURE EFFECTS

As the results have shown, exposure of the graphite-epoxy prepreg to high humidity conditions at both ambient and elevated temperatures causes complex changes in the reactivity of the prepreg. First, the material showed a slowing of the relative reaction rate. Then, after longer aging periods, a decrease in the activation energy of samples exposed to high humidity conditions was observed accompanied by increased relative reaction rates. The time required before these changes were observed was dependent on the aging temperature, occurring sooner for samples aged at higher temperatures.

Curve 717850-A

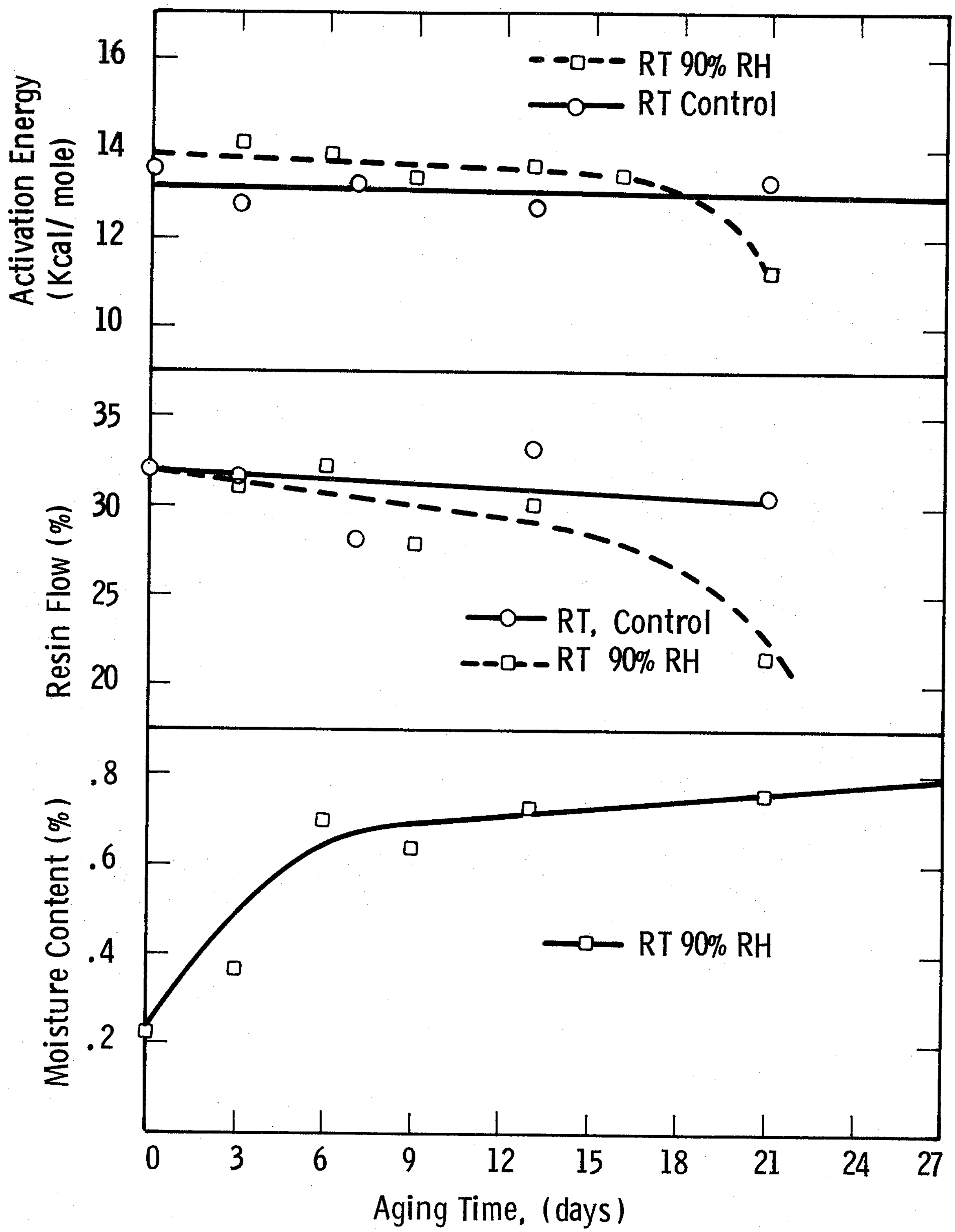


Fig. 32 — Activation energy, resin flow, and moisture content for 3501-6/AS prepreg aged at room temperature (RT)

Curve 717852-A

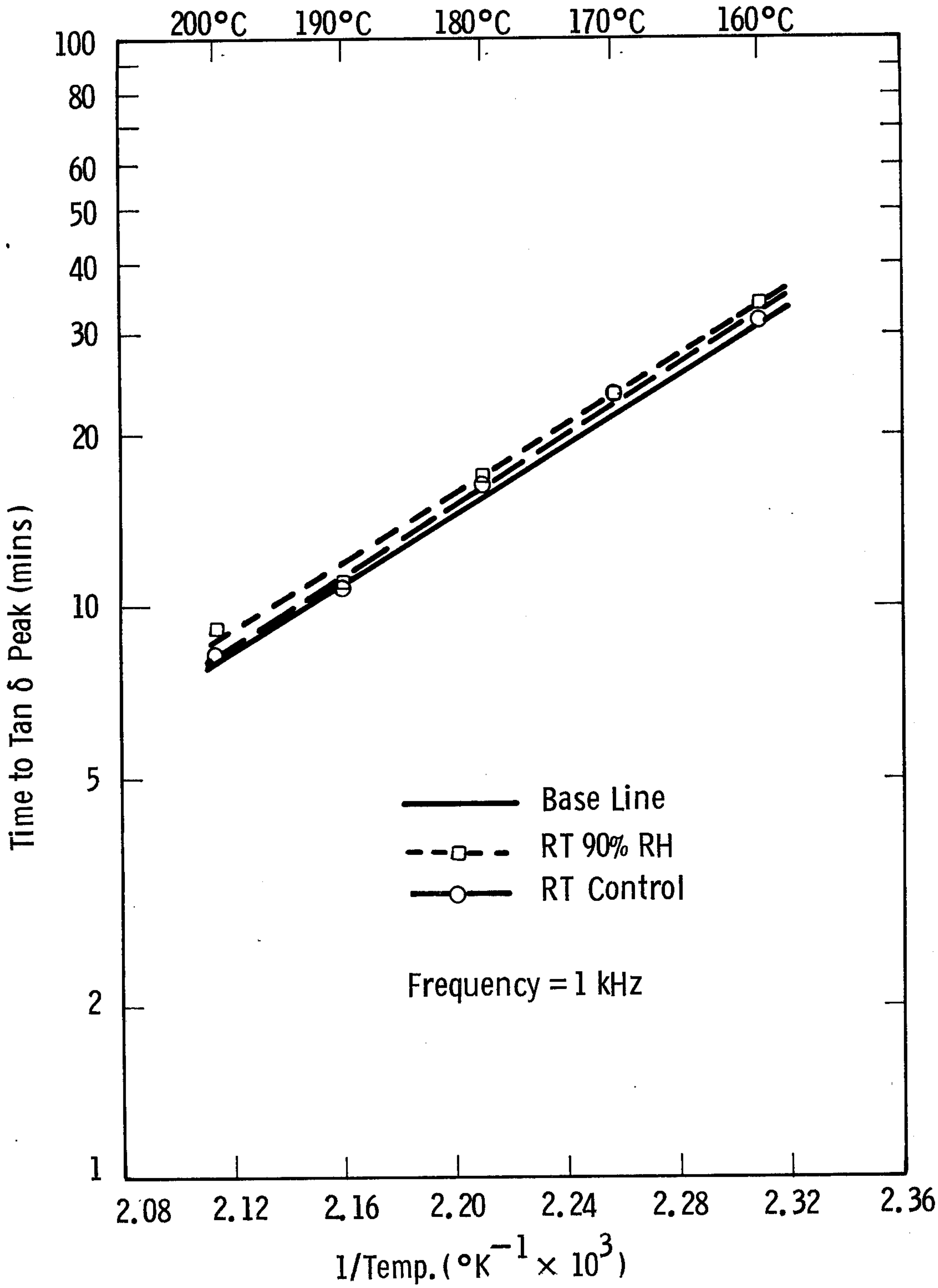


Fig. 33— Arrhenius plot for the reaction of the prepreg after aging 6 days at room temperature (RT)

Curve 717851-A

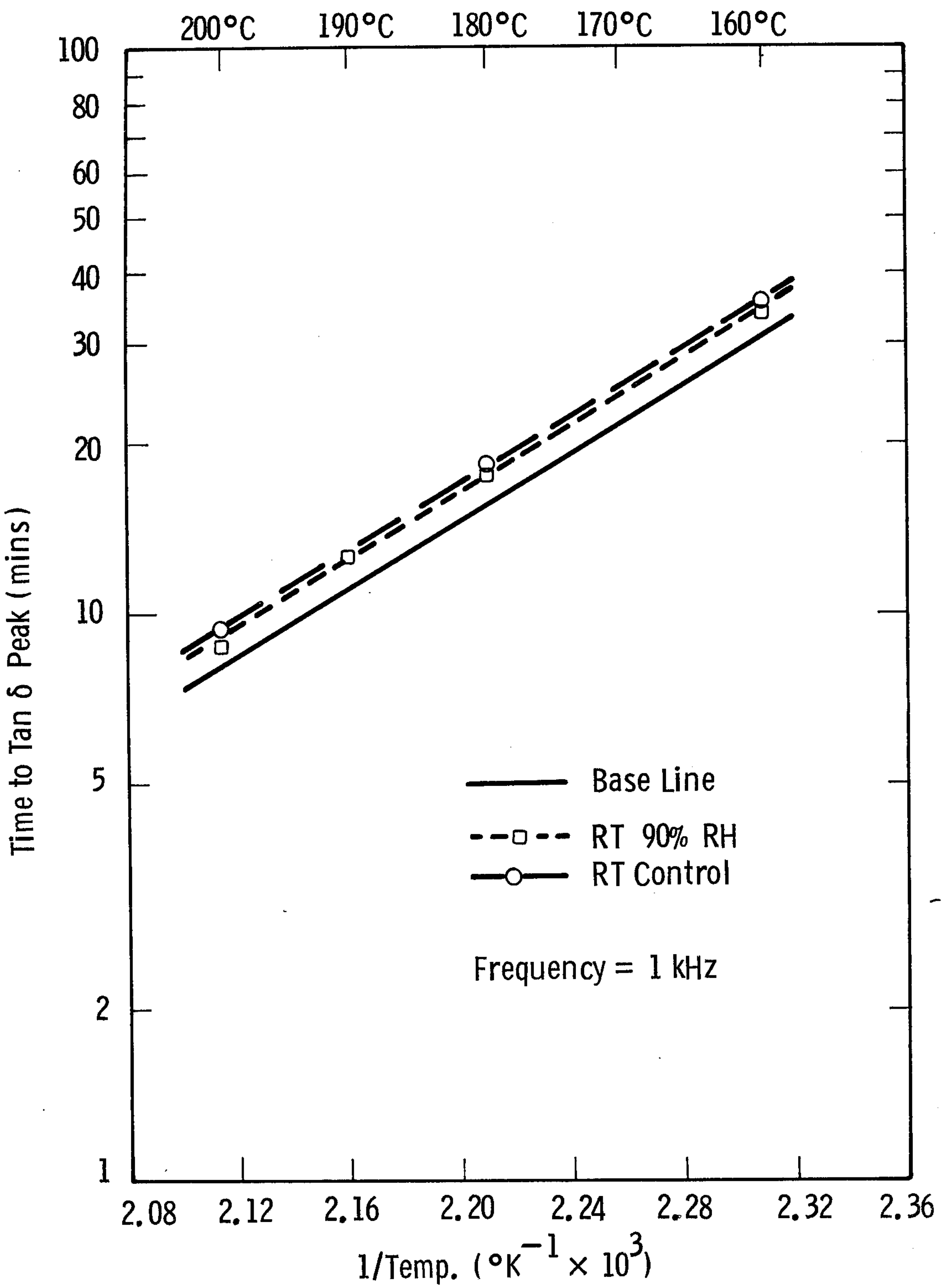


Fig. 34 — Arrhenius plot for the reaction of the prepreg after aging 13 days at room temperature (RT)

Curve 717864-A

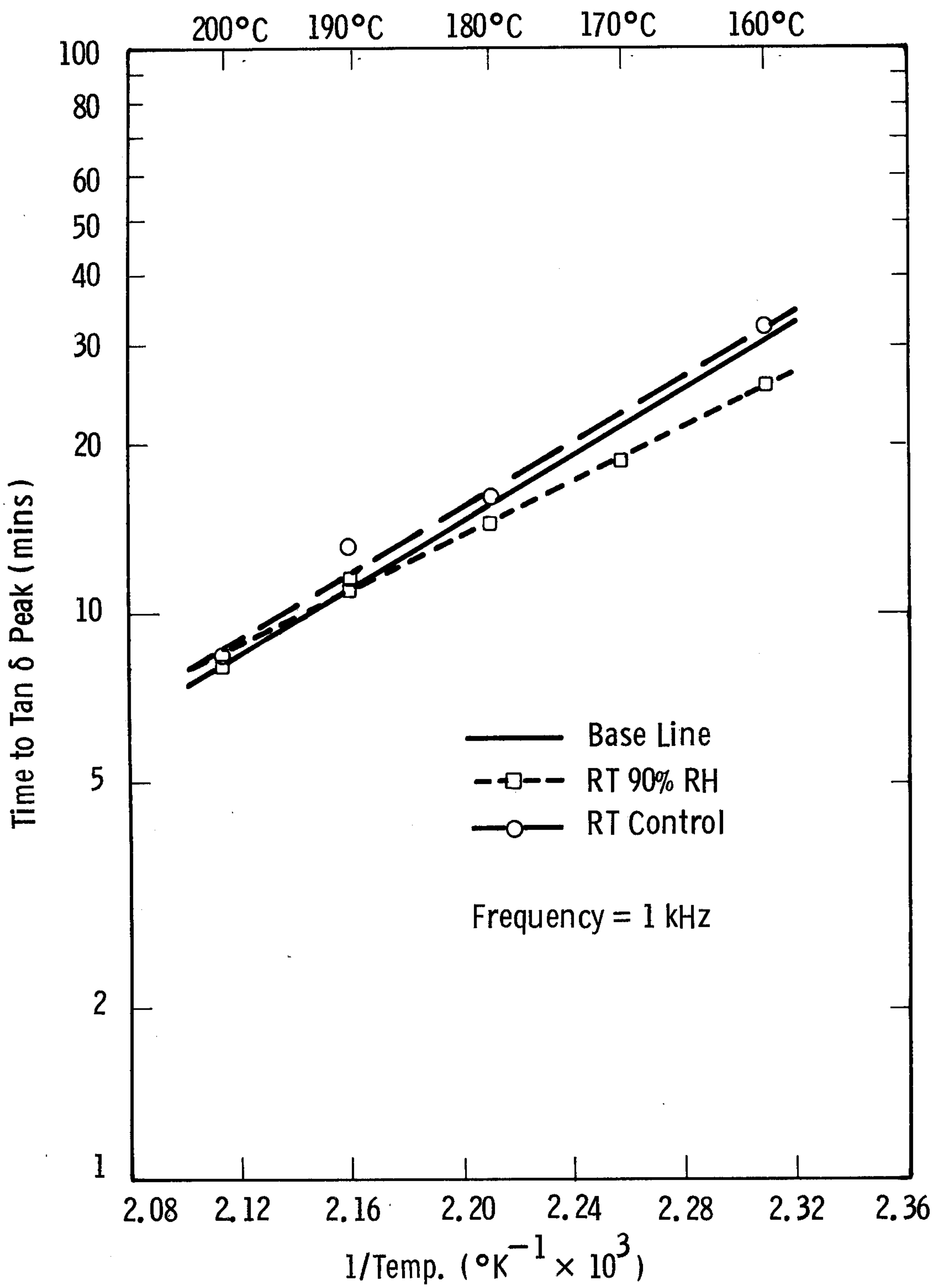


Fig. 35 – Arrhenius plot for the reaction of the prepreg after aging 21 days at RT

The decrease in relative reaction rate, as is best seen in Figures 24, 29 and 34 for each of the aging conditions, occurs with both the control and humidity aged samples. Previous work has shown that one type of $BF_3$ catalyst commonly used in epoxy chemistry ($BF_3$·MEA) reacts slowly with water to form ethylammonium tetrafluoborate and hydroxy fluoborates. The hydroxy fluoborates are ineffective catalysts and are insoluble in some epoxy resin systems. Thus, hydrolysis of the catalyst can result in sluggish catalytic activity[4], accounting for the initial decrease in reaction rate of the prepreg. The source of the water causing the catalyst hydrolysis in the humidity aged samples was the environment. However, the reason for the decreased reaction rate in the control samples was perplexing until it was realized that the 0.22% (by weight) moisture initially in the prepreg was not removed prior to aging. Apparently this small amount of moisture is sufficient to decrease the effectiveness of the catalyst. To verify this hypothesis, samples were first dried for two days in an evacuated desiccator and then aged for two days at 120°F under control conditions. The Arrhenius plot for these predried samples, Figure 36, was coincidental with the base line (for unaged prepreg), indicating no change in the reactivity of the prepreg had occurred. The Arrhenius plot for prepreg aged under control conditions without predrying (as in Figure 24) is also given in Figure 36. It displays a significantly decreased reaction rate compared to that of the predried samples. Figure 37 which shows similar data for samples aged 4 days at 120°F, confirms the hypothesis.

Although a slowing of the relative reaction rate was noted for samples aged under both control and humid conditions, only humidity aged samples showed an eventual decrease in activation energy. Accompanying this decrease in activation energy was a greatly increased reaction rate at lower cure temperatures (160°, 170°C), as shown clearly in Figures 26, 31 and 35 for each of the aging conditions. The results indicate that the cause of this increased reactivity is moisture absorbed from the environment. As was discussed by I. T. Smith, the moisture in the prepreg will serve as a proton donor to catalyze the reaction between the epoxide

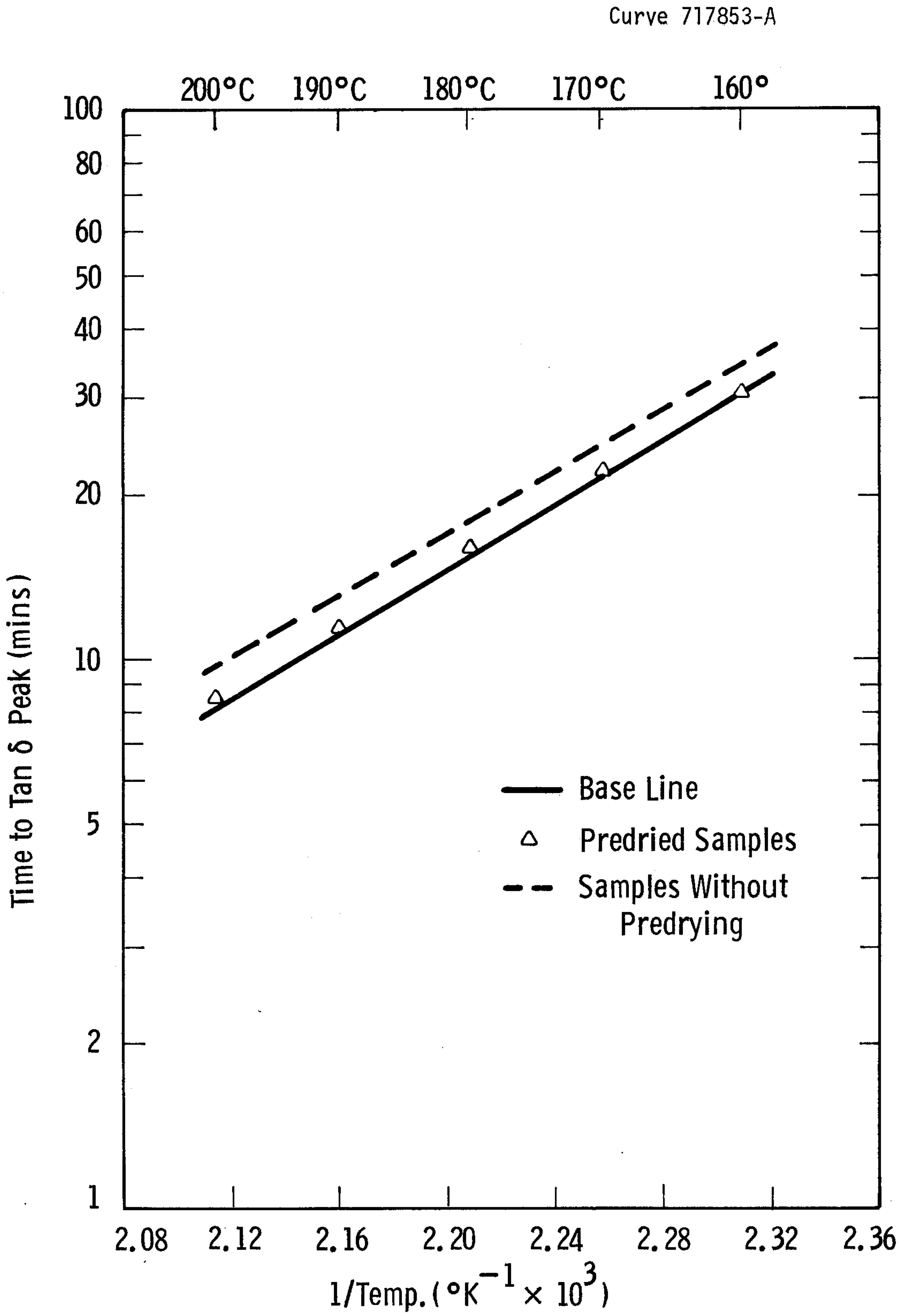


Fig. 36 — Arrhenius plot for the reaction of the prepreg after aging 2 days at 120°F. Control samples with and without predrying

Curve 718223-A

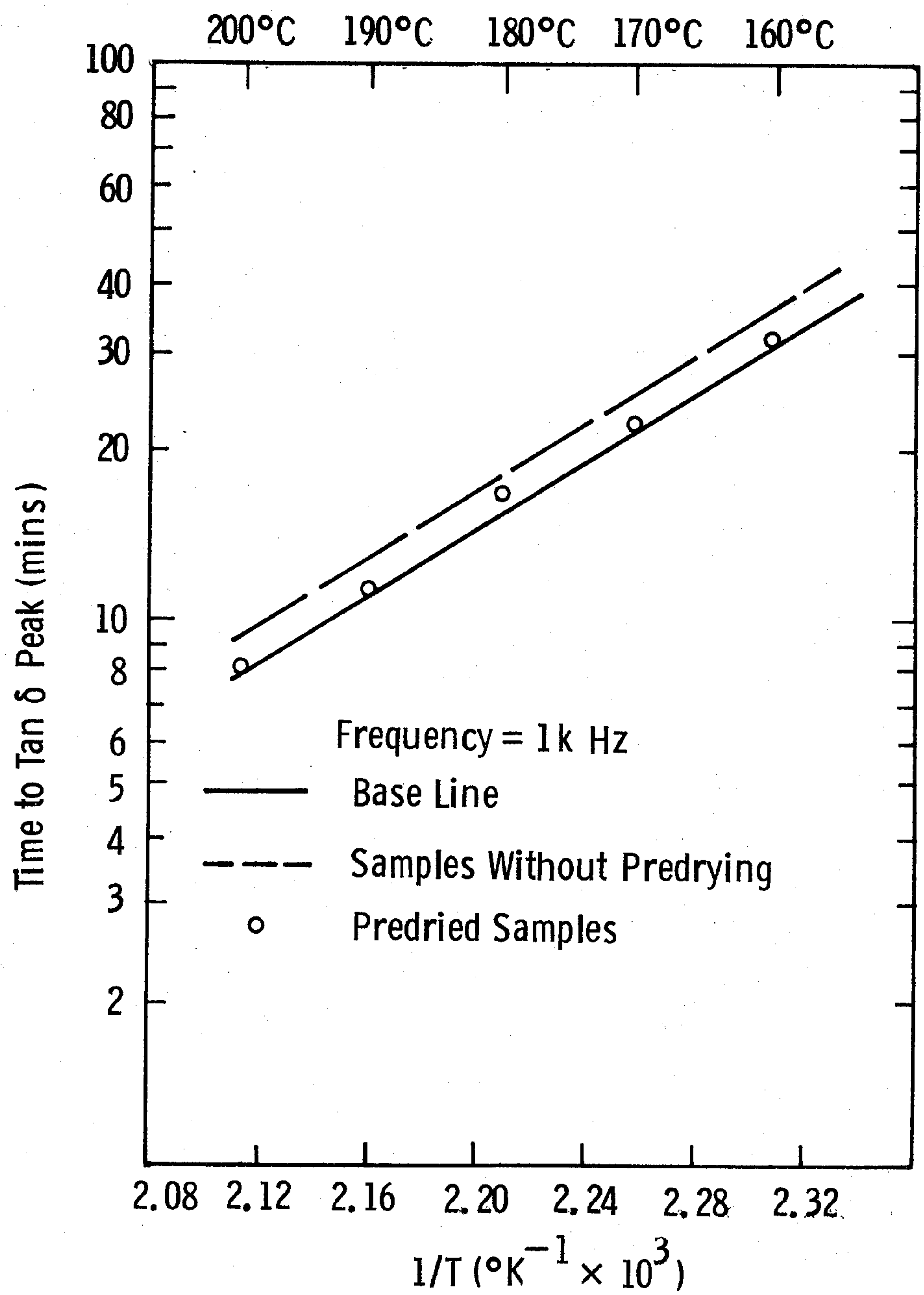


Fig. 37 — Arrhenius plot for the reaction of the prepreg after aging 4 days at 120°F. Control samples with and without predrying

and the aromatic-amine.[9] The observed changes in the reactivity of the prepreg indicate that water is a more effective catalyst than the $BF_3$ catalyst, especially at lower cure temperatures.

In previous work, Hinrichs, et al., observed that changes in the reaction rate of 5208 graphite-epoxy prepreg material due to aging five days at room temperature, 98% RH were reversible.[4] That is, when the 5208 prepreg was dried to its original moisture content, its original reactivity was regained. However, our data clearly shows that aging 3501-6/AS prepreg under high humidity conditions (>80% RH) eventually leads to irreversible changes in reactivity, depending on aging time and temperature. The fact that the changes in reactivity were found to be irreversible suggests that some moisture was complexed in the resin during aging under humidity and this moisture was not removed by desiccation.

Liquid chromatography (LC) also used to verify the increased reactivity of the prepreg, showed that samples aged under humid conditions contained much less monomer than those aged under control conditions, indicating greater prepreg reactivity in a moist environment.

The LC analysis confirmed the increased reactivity of humidity-exposed prepreg, while the dielectric analysis indicated that these moisture effects are irreversible. The increased molecular weight of the resin during humid aging would account for the decreasing of the Arrhenius line toward shorter tan $\delta$ times. However, this would not explain the change in activation energy (slope of the Arrhenius line). Because the same reaction product was obtained by aging in both humid and control conditions, it can be concluded that the same overall reaction is occurring but via different mechanisms.

## 5.5 SUMMARY OF MOISTURE EFFECTS

In summary, it has been shown that exposing the graphite-epoxy prepreg to humid environments leads to increased reactivity at cure temperatures below the final temperature (180°C) used for curing during the manufacturing cycle. The extent to which the reactivity is increased is

dependent on the temperature and humidity of the environment, as well as the period of exposure. At room temperature and 90% RH, 16 days are required before any significant changes are seen. However, at 120°F and 80% RH, considerable changes are found in only two days.

It may be hypothesized that a faster cure rate would result in a composite with excessive resin content and an increase in the number of voids. Volatiles which would normally escape during curing would be trapped by the quickly gelling resin. The overall effect would be decreased strength and performance of the composite. Such a hypothesis, however, needs to be confirmed by testing of laminates made from prepreg aged under dry and humid conditions.

## 6. CONCLUSIONS

1. A device which integrates time and temperature of exposure provides a practical, easy to use and inexpensive method to indicate an overage condition for prepregs. Called a Time-Temperature Watch (TTW), its readings correlate well with prepreg age (within limited temperature ranges). Using the Type 33 TTW, an overage condition is reached for 3501-6/AS prepreg when the device shows a reading of $5 \pm 1$.

2. Such devices perform no test on the material and are therefore ideally suited for field and on-board ship use when test facilities may not be present. However, they do have to be carried with the material at all times.

3. Another such device called the Monitormark, in its present configuration, is not a suitable overage indicator for thermosetting products. It does have the advantage of greater humidity resistance than the TTW.

4. Dielectric analysis (DA) and dynamic mechanical analysis (DMA) are both easy-to-use, practical methods whose readings correlate well with prepreg age and provide a critical value which indicates an overage condition.

5. For DA the critical value is given by measuring the temperature of the first peak in dissipation factor at a frequency of 1 kHz. For 3501-6/AS this critical value is 64 $\pm$ 2°C at which point the end of the useful life of the prepreg is reached.

6. For DMA the critical value is given by measuring the temperature of the peak in relative damping. For 3501-6/AS this critical value is 32 $\pm$ 3°C at which point the end of the useful life of the prepreg is reached.

7. Both DA and DMA, which require the use of analytical equipment and are therefore not as convenient to use as the TTW, are more accurate than the TTW.

8. Exposure to a humid environment produces complex changes in the reactivity of 3501-6/AS graphite-epoxy prepreg. The rate of change is temperature dependent.

9. Exposure to humidity for a short period of time produces a small reduction in the reactivity of the prepreg which may be attributed to hydrolysis of the Lewis acid catalyst. This change is probably not significant from a processability standpoint.

10. A much more significant change occurs with prolonged humidity exposure and results in much faster reactivity of the prepreg, particularly at temperatures below recommended final cure temperature. This is the result of a change in curing mechanism as indicated by the considerably decreased activation energy of the prepreg reaction.

# 7. RECOMMENDATIONS

1. Aging studies should be performed on the 3501-6/AS prepreg with known small changes in chemistry. The purpose of this would be to determine the effect (if any) of chemical changes on the aging of the prepreg and the age indicating methods.

2. Aging studies should be initiated on adhesives and sealants, to develop overage indicators for them.

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# Westinghouse R&D Center
# TECHNICAL DOCUMENT SUMMARY



**Document No.:** 79-9B7-PPREG-R2 **Date:** Sept. 28, 1979

**Title:** OVERAGE INDICATOR FOR GRAPHITE FIBER EPOXY PREPREG

**Author(s):** Z. N. Sanjana

**Department:** Polymers & Plastics

**Sponsor:** Naval Air Systems Command

**Pages:** 66 **References:** 9 **Keywords:** dielectric, graphite, epoxy, B-stage, prepreg, dynamic, analysis/structure, time, differential, analysis/composition, indicators, scanning, calorimetry, temperature, integrators, mechanical, aging, humidity

**SUMMARY (Purpose, Scope, Approach, Results, Conclusions, Significance):**

This work was sponsored by the Naval Air Systems Command to develop overage indicators for graphite-epoxy prepregs. Aging of Hercules 3501-6/AS graphite-epoxy prepreg under diverse temperature and humidity conditions was used to determine that dielectric analysis, dynamic mechanical analysis and a time-temperature integrator are effective overage indicators. The value of each of the indicators which relate to an overage condition for this prepreg are specified.

The effect of humidity exposure on the prepreg was also investigated It was shown that aging under humid conditions enhances the reactivity of the prepreg at temperature below final cure temperature (180°C). The enhanced reactivity is irreversible, is a function of time and temperature of exposure, and of the RH of the environment to which the prepreg is exposed.

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